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STUDIES OF AN IONOMER:

SULFONATED POLYSTYRENE SALTS IN BULK AND SOLUTION

A Dissertation Presented

by

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Robert W. Lenz, Member

Edwin L. Thomas

Edwin L. Thomas, Member

Department Head

Polymer Science & Engineering

We live, dying is not our business,
shame is another lost episode,
but like an unseen madonna, conscience
is standing at every crossroad.

Yevgeny Yevtushenko
to D. Shostakovich

Dedicated to Grant John Gorton I and Walter Phelps Warren II

in whose memory dwell insight and perspective.

ACKNOWLEDGMENTS

Encouragement and advice from several friends and scientists deserves mention here. It is a pleasure to acknowledge the members of my dissertation committee and, in particular, my thesis advisor Professor William MacKnight. Any merit which this study may possess is due in large part to his foresight and scientific acumen.

This study bears the impact of several other scientists as well. It has been truly enjoyable to collaborate with Drs. Sunil Sinha and Dennis Peiffer of the Exxon Research & Engineering Company, Professor Julia Higgins of Imperial College, and Dr. Robert Lundberg of the Exxon Chemical Company. I am particularly indebted to Sonny for his patience with sludge physics. It is also a pleasure to recall many helpful discussions with Drs. Tom Witten, Phil Pincus and Bill Graessley.

The years in Amherst have been greatly enriched by the comradery of my fellow graduate students. I would like to thank them as a whole for their spirited friendship. It is a particular joy to acknowledge Francois Chambon as both a friend and scientist. I am also grateful to J.Michael Connolly for his experimental assistance and stimulating discussion. A final word of gratitude is due my family, in particular to my sister Martha, for their constant support and strength.

PREFACE

The research for this dissertation has involved studies of ion-containing polymers and is presented in two sections which may be read independently. Solution properties of ionomers are investigated and discussed in Chapter I. Thermal and mechanical studies of ionomers in the solid state form the basis for Chapter II. The common thread which unites these experiments is the material studied. Salts of lightly sulfonated polystyrene have been used as a model system in this search for the molecular basis of ionomer behavior in bulk and solution.

ABSTRACT

STUDIES OF AN IONOMER:

SULFONATED POLYSTYRENE SALTS IN BULK AND SOLUTION

February 1987

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Rheological properties of flexible long chain polymers can be dramatically altered by introducing a very small fraction of ionic groups along the hydrocarbon backbone. The molecular parameters responsible for the solution properties of lightly sulfonated polystyrene ionomers have been studied in both an ionizing and a non-ionizing solvent. A combination of solution viscosity measurements, quasi-elastic light scattering, static small-angle light scattering and small-angle neutron scattering studies have been performed. The results yield values for the effective diffusion coefficient, radius of gyration and apparent molecular weight. From this combination of scattering and rheological information, a more detailed description emerges of ionomer solution behavior over a range of solvent polarities, polymeric

molecular weights, ionic contents and concentrations. When dissolved in ionizing solvents, ionomers mimic classical polyelectrolytes by displaying chain expansion at low concentrations. When the same ionomeric material is dissolved in a non-ionizing solvent however, single chains aggregate into microgel particles without significant change in individual coil size.

Ionomers in the solid state are of fundamental scientific and technological interest. Thermal relaxations in bulk ionomers can be directly related to morphological features. To study these relaxations, a model ion-containing polymer system has been developed and characterized. Lightly sulfonated polystyrene ionomers of both broad and narrow molecular weight distribution have been studied by elemental analysis, gel permeation chromatography, thermogravimetric analysis and small-angle x-ray scattering. The presence of thermal transitions and relaxations has been determined by differential scanning calorimetry and dynamic mechanical thermal analysis. The results show that clustering occurs in sodium-based ionomers. The onset of clustering occurs at lower ionic concentrations than in comparable carboylate-based ionomers and is relatively insensitive to the distribution of backbone molecular weights.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I. SOLUTION STUDIES

INTRODUCTION

Perhaps the oldest branch of polymer science is the study of ion-containing polymers since most naturally occuring polymers contain ionic species. The area of structure-property relationships for synthetic polymer materials containing salt groups has seen expansive growth in recent years. This is evident from the scientific interest manifested in the technical literature and by the appearance of several monographs devoted to the subject.[1-8] Clearly, the range of polymeric materials within the field of ionic polymers is extremely varied, extending from naturally occuring biopolymers all the way to ceramics and inorganic glasses. The class of materials to be discussed here occupies an intermediate position between purely organic structures on the one hand and purely inorganic structures on the other. The term **ionomer** was coined by the DuPont Co. to describe such materials and has come into general use to mean a polymer which is composed of a hydrocarbon backbone containing pendant acid groups which are neutralized partially or completely to form salts. The concentration of the salt groups may vary but the hydrocarbon backbone is always the majority component. In general, unless otherwise specified, the term ionomer will refer to polymers containing less than ten mole percent salt groups. This

specifically excludes polyelectrolytes, which contain salt groups on alternate backbone atoms.

Considerable industrial and academic research effort has been expended on ionomers in the solid state. A brief historical sketch of these bulk studies will be presented as background for the ensuing solution studies. Despite extensive study, several questions in the field of ionomers remain unanswered.

The introduction of ionic groups to hydrocarbon resins dates back to the 1930's when methods for the carboxylation of elastomers appeared in the patent literature. In the 1950's, B.F. Goodrich introduced one of the first elastomers based on ionic interactions - a poly(butadiene-co-acrylonitrile-co-acrylic acid). These materials could be neutralized with zinc salts and plasticized to break ionic association at elevated temperature. Such ionic elastomers displayed enhanced tensile properties and improved adhesion compared to conventional copolymers.

A second family of ionic elastomers was introduced in the 1950's by E.I. DuPont de Nemours & Co. under the tradename Hypalon®. These materials were based on the sulfonation of chlorinated polyethylene. After suitable curing with various metal oxides, these materials possess a combination of ionic and covalent crosslinks. Upon neutralization, these polyethylene-based materials change from a material with the general properties of low-density polyethylene to an extremely tough,

flexible, and optically clear thermoplastic. This dramatic change in properties was initially understood on the basis of ionic interactions. It seemed natural to assume that these elastomeric properties were due to the presence of ionic crosslinks. Such crosslinks were originally envisioned as a divalent cation bridging two pendant anionic groups. Subsequent work with monovalent species led to the realization that the "ionic crosslinks" possess a more complicated structure. Factors such as the coordinating tendency of the counterion, the low polarity of the hydrocarbon backbone, and the influence of polar impurities such as water have to be considered. On closer examination, it was found that the early simplified concept of the ionic crosslink was inadequate.

A breakthrough occurred in the mid-1960's when DuPont introduced poly(ethylene-co-methacrylic acid) under the tradename Surlyn®; these copolymers were partially neutralized with sodium and zinc cations. These modified polyethylenes possess remarkable clarity and tensile properties superior to those of conventional polyethylene. The development of Surlyn® was an important factor in stimulating research in ionomers. The Surlyn® systems emphasized the versatility of ionomer structure and the unique properties available from the modification of the polyethylene backbone. Many of the features which are peculiar to ionomers were recognized at this time; notably, the idea that multi-ion clusters would be formed due to the low dielectric constant of the hydrocarbon matrix. It was only with more detailed x-ray diffraction

studies and mechanical property measurements that the morphology of these materials was gradually revealed.

During the 1970's and 1980's, several novel ionomer systems have been developed. Of particular interest are the perfluorinated resins and halato-telechelic polymers as well as the various sulfonated materials. This study is focused on the solution behavior of one of these materials, sulfonated polystyrene.

In comparison with the extensive studies of ionomers in the solid state, ionomers in solution have received remarkably sparse attention. At the current time, only solution viscosities have been investigated. Given the dual nature of ionomers (that is, the combination of polar and nonpolar species in the same macromolecule) it is understandable that dissolution is often difficult to achieve.

In pioneering viscometric studies by Lundberg and Makowski[9], this problem of dissolution was solved by the use of mixed solvents. Solutions of sodium compensated sulfonated polystyrene in a xylene/alcohol mixture exhibit unusual solution viscosity behavior. At relatively low solute concentrations, these ionomers display unexpected thickening behavior in nonpolar organic solvents. This phenomena is explained by association of the ionic groups. Upon addition of modest levels of polar cosolvent, the solution viscosity drops considerably. The viscosity of these resulting solutions displays an unusual

temperature dependence. Remarkably, solution viscosity increases with temperature.

These effects can be explained by a temperature-dependent interaction between the polar cosolvent and the sulfonate groups. This interaction is simplified as:

$$\underset{\text{associating form}}{\text{alcohol} + (\text{P-SO}_3\text{Na})_n} \rightleftharpoons \underset{\text{solvated form}}{n(\text{alcohol-P-SO}_3\text{Na})}$$

where the solvated form is favored at high temperature.

Further viscometric investigations by Lundberg and Phillips[10] reveal similar behavior for sulfonated polystyrene salts dissolved in the single low polarity solvent tetrahydrofuran. The solution viscosities observed in this low dielectric medium are consistent with the earlier mixed solvent results and can be explained in terms of ion pair associations.

When sulfonated polystyrene salts are dissolved in a medium of high dielectric constant, however, polyelectrolyte behavior is observed. This is manifested by a dramatic upsweep in viscosity at low polymer concentrations. Polyelectrolyte behavior can also be induced in low polarity solvents by the addition of a polar cosolvent. This variation

between associating and polyelectrolyte behavior can be understood as a variation between ion pair and free ion behavior respectively.

The generality of these phenomena is demonstrated by the work of Niezette et al.[11] They observed that solutions of n-butyl methacrylate/ methacrylic acid salts in toluene and dimethyl formamide behave as associating and polyelectrolyte solutions respectively. The results of Salamone et al.[12] from solutions of ampholytic styrene ionomers in xylene/alcohol mixtures are also consistent with Lundberg's findings. Salamone's copolymers of styrene and 3-methacrylamido-propyltrimethyl ammonium 2-acrylamido-2-methyl propane sulfonate show extensive intermolecular ionic interactions in benzyl alcohol as well.

A third corroborating example is the work of Lundberg[13] using sulfonated ethylene propylene diene terpolymers. When these rubber salts are dissolved in xylene/alcohol mixtures, the solution viscosity behavior is analogous to that of sulfonated polystyrene salts in mixed solvents. In this study, the important distinction between intra- and inter-chain associations is made. In media of low polarity, associations may occur either between ionic groups along the same macromolecular chain or between ionic groups of different chains. This balance between intra- and inter-chain effects was investigated by Lundberg and Phillips[14] in their study of sample history effects. These results reveal a combination of inter- and intra-chain associations in sulfonated polystyrene ionomers which results in a restriction of the

entanglement/disentanglement equilibrium in solvents of low polarity. This restricted equilibrium strongly affects the properties of the resulting ionomer solution. These results warn of the importance of consistent sample preparation.

In summary, the field of ionomer solutions remains largely unstudied. An important early result is the discovery of two types of solution viscosity behavior: associating and polyelectrolyte. The unique solution viscosity of ionomers must arise from the molecular behavior of the polymer chains. The molecular conformation of an ionomer chain in solution is determined by a complicated balance of forces. These forces can include charge repulsion and screening, van der Waals interactions and the entropic driving force for mixing as well as chain elasticity. As a result, the molecular conformation and hence the solution properties of ionomers are expected to vary with solvent, ionic content and type, temperature and history, polymer molecular weight and concentration. As mentioned above, solvent polarity plays a major role in determining the solution viscosity behavior of flexible chain ionomers. Hence the solution properties of ion-containing polymers naturally divides into two categories: ionizing and non-ionizing solvent systems.

Investigation of these two classes of ionomer solution behavior was undertaken using a variety of scattering techniques. Although the long-range goal is an understanding of ionomer solutions over the complete

range of environments, this study is restricted to a single class of ionomers: sulfonated polystyrenes (SPS) of narrow molecular weight distribution containing less than ten mole percent ionic groups. Specifically, the effects of solvent type, molecular weight, sulfonation level, counterion and concentration have been examined. The results establish a molecular basis for the solution viscosity behavior of SPS in both ionizing and non-ionizing environments. It is expected that this study of a model system will be relevant to other sulfonate ionomers in particular and to ionomer solutions in general with appropriate considerations for backbone architecture and counterion structure.

EXPERIMENTAL

Sample preparation. Anionically polymerized stryene and perdeutriostyrene were purchased from Polymer Laboratories Ltd and Pressure Chemical Corporation for these studies. These polymers had number average molecular weights of 3.50×10^4, 5.00×10^4, 1.00×10^5, 1.15×10^5, 9.00×10^5, and 1.80×10^6 Daltons with polydispersities less than 1.05 in all instances.

The sulfonated polymers were prepared by procedures similar to those described previously.[15,16] This work was performed by the Exxon Research & Engineering Company. In general, these polymers were modified in 1,2 dichloroethane using acetyl sulfate as the sulfonating agent. Following reaction at 50°C, the polymers were neutralized with either sodium or zinc acetate and precipitated into water/methanol mixtures. The solutions were subsequently filtered and the polymer isolated as either the free acid or the sodium or zinc salt via stream stripping. The sulfonated polymer was dried for 24-48 hours at 80°C. The sulfur content of the polymers was determined analytically and used to calculate the sulfonate content.

The sulfonated polystyrenes ranged in sulfonate content from about 0.50 to 9.6 mole percent. In this nomenclature, sulfonate content is

based on the average repeat unit of the polymer chain. Therefore, in the case of polystyrene, 1 mole percent refers to an average of one out of every hundred repeat units functionalized. A compilation of the materials studied is given in Table 1.

Polymer solutions were prepared volumetrically using magnetic stirrers for agitation. Freshly opened solvents were used as received to prepare stock solutions for serial dilution. These solutions were stirred for a minimum of 24 hours before dilution to ensure complete dissolution. Prior to use in light scattering measurements, the solutions were carefully filtered through 0.5 and 0.2μ filters.

The reduced viscosity [defined as $(\eta-\eta_0)/\eta_0 c$ where η is the viscosity of the polymer solution, η_0 is the viscosity of the solvent and c is the polymer concentration] was measured with a standard Ubbelodhe viscometer. These measurements were provided by the Exxon Engineering & Research and Exxon Chemical Companies. Viscosity measurements were made at $25\pm0.5^{\circ}C$ in a thermostatted bath. Reproducible flow rates were obtained and the measurements were repeated (typically five times) with the average value given in the text. No shear rate effects were observed within the shear rate range of interest.

Table 1. Sodium Salts of Sulfonated Polystyrene for Solution Studies.

Molecular Weight (g/mol)	Sulfonation wt%S	Sulfonation mol%S	Exxon Sample ID
35,000	0	0	
35,000	0.007	1.0	11868-26A
35,000	1.02	4.2	11868-26B
35,000	1.52	7.3	11868-26C
50,000	0	0	
50,000	0.009	0.4	11868-26D
50,000	1.50	5.2	11868-26E
50,000	1.93	8.1	11868-26F
100,000	0	0	
100,000	0.35	1.15	11868-104A
100,000	0.91	3.05	11868-104F
100,000		4.2	
100,000	1.39	4.75	11868-104B
115,000	0	0	
115,000		1.1 *	10563-126A
115,000		2.49 *	12169-95
115,000		3.6	10563-126B
115,000		9.6	10563-126C
900,000	0	0	
900,000	0.15	0.50	11868-42D
900,000	0.52	1.72	11868-52F
900,000	0.95	3.20	11868-52C
1,800,000	0	0	
1,800,000	0.21	0.68	11868-52H
1,800,000	0.70	2.30	11868-42B
1,800,000	1.14	3.80	11868-42A

* Zinc, sodium and acid forms

Light scattering measurements. A Chromatix KMX-6 low angle laser light scattering photometer was used in all static light scattering measurements. This apparatus includes a He-Ne laser of wavelength 633 nm, a silica cell, a series of annuli to determine the forward scattering angle and a highly linear photomultiplier. The 6-7^{o} annulus was used for the measurements reported here. A Chromatix KMX-16 laser differential refractometer was used to measure the refractive index increments. These measurements were made at a temperature of 25^{o}C.

A Brookhaven Instruments BI-2030 with a digital correlator was used in the quasi-elastic light scattering measurements. Again a He-Ne laser (Spectra Physics Model 124B) operating at 35 mW power with a wavelength of 633 nm was used as the light source. Measurements were made at 25^{o}C and a scattering angle of 90^{o}. Sample and duration times were adjusted to give reproducible results for each solution.

Neutron scattering measurements. Small-angle neutron scattering measurements were performed at three locations: the Institut Laue Langevin (ILL) in Grenoble, the Brookhaven National Laboratory (BNL) in New York, and the Oak Ridge National Laboratory (ORNL) in Tennessee. It is a pleasure to acknowledge the assistance of several scientists in performing these neutron scattering measurements: Drs. A. Rennie and A. Wright of ILL, D. Schneider and S. Shapiro of BNL, and G. Wignall of

ORNL. Without their expertise, these measurements would not have been possible.

At ILL, the D11 spectrometer[17] was used with a wavelength of 8 A and a sample-to-detector distance of 10 m. The H-9 spectrometer[18] was used at BNL with a sample-to-detector distance of 19 m and a 7.5 A wavelength. Neutrons of 4.75 A wavelength and a sample-to-detector distance of 4 m were chosen at ORNL. A directory of these experiments is given in Table 2. In all experiments, the polymer solutions were held in tightly-capped quartz cells with the sample area defined by circular diaphragms. The incoherent scattering from a water sample under identical conditions was used for detector normalization. Background corrections were made by subtracting the scattering due to the cell and solvent. Standard corrections for sample transmission were also made. In the ILL and ORNL experiments, scattering from the polymer solutions was measured at higher angles and used to estimate the incoherent scattering.

Table 2. Directory of SANS Experiments.

A. Studies of Na-SPS in THF(D6)

Materials	Concentrations	Laboratory
100,000 g/mol; 4.2 mol%S	0.5 to 4.0 g/dl	ILL March 21 & 25, 1986
100,000 g/mol; 0 mol%S	0.5 g/dl	ILL March 21 & 25, 1986

B. Studies of Na-SPS in DMF(D7)

Materials	Concentrations	Laboratory
115,000 g/mol; 0 to 9.6 mol%S	0.5 g/dl	BNL March 2 - 6, 1984 June 12, 1984
100,000 g/mol; 0 & 4.2 mol%S	0.5 to 4.0 g/dl	ORNL January 31, 1985 to February 5, 1986
50,000 g/mol; 0 to 8.1 mol%S	0.5 g/dl 0.2 to 4.0 g/dl	BNL August 2-7, 1984 ORNL January 31, 1985 to February 5, 1986
35,000 g/mol; 0 to 7.3 mol%S	0.5 g/dl 0.5 to 4.0 g/dl	BNL August 2-7, 1984 ORNL January 31, 1985 to February 5, 1986

THEORY AND ANALYSIS

Static Scattering

The intensity of radiation scattered by a polymer solution may be measured as a function of either solution concentration or scattering angle. In the neutron scattering experiments of this study, the angular variation was measured. The intensity of scattered neutrons at a given scattering angle θ is determined as the radially averaged scattering at a distance d from the neutron beam center. The angle θ is defined by d/D where D is the sample-to-detector distance. The scattering vector $\mathbf{q}$ is then calculated as

$$|\mathbf{q}| = \frac{4\pi}{\lambda}\sin(\theta/2) \sim \frac{2\pi}{\lambda}\frac{d}{D} \qquad (1)$$

where λ is the wavelength of the incident neutrons.

The intensity of radiation scattered by a polymer solution is determined by the scattering power or contrast factor 'a' and the spatial arrangement of scatterers. The angular dependence of the scattered intensity $I(\mathbf{q})$ is determined by the following summation.

$$I(\mathbf{q}) = K \sum_{i,j;\alpha,\beta,} a_{i\alpha} a_{j\beta} \exp[i\mathbf{q}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})] \qquad (2)$$

In equation 2, the summation indices i and j refer to individual monomers which are located along chains α and β. The separation between scatterers i and j is given by the vector distance $\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta}$. In the case of neutron scattering, the contrast factor is reported as a scattering cross-section. The large difference in neutron scattering cross-section between hydrogen and deuterium is used. The factor K contains molecular weight terms and machine parameters.

The contrast factor $a_{i\alpha}$ is calculated relative to the solvent and can be described as the average contrast $\bar{a}$ plus the local deviation from the average $\delta a_{i\alpha}$. That is,

$$a_{i\alpha} = \bar{a} + \delta a_{i\alpha} \tag{3}$$

substituting this relationship into equation 2 yields the following collection of sums for a solution which contains both hydrogenous (H) and perdeuterated (D) polymers.

$$I(\mathbf{q}) = K\bar{a}^2 \sum_{i,j;\alpha,\beta} \exp[i\mathbf{q}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})] + K[\delta a_{i\alpha}^{\ 2} + \delta a_{j\beta}^{\ 2}] \sum_{i,j;\alpha,\beta} \exp[i\mathbf{q}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})] \tag{4a}$$

This collection of sums reduces to

$$I(\mathbf{q}) = K\bar{a}^2 \sum_{i,j,\alpha,\beta} \exp[i\mathbf{q}(r_{i\alpha} - r_{j\beta})] \qquad (4b)$$

$$+ K[C_H \delta a_H^2 + (1-C_H)\delta a_D^2] \sum_{i,j} \exp[i\mathbf{q}(r_i - r_j)]$$

A more familiar way of writing equation (4b) is

$$I(\mathbf{q}) = K\bar{a}^2[f(\mathbf{q}) + s(\mathbf{q})] + K[C_H \delta a_H^2 + (1-C_D)\delta a_D^2] f(\mathbf{q}) \qquad (4c)$$

where $f(\mathbf{q})$ is the single chain scattering form factor and $s(q)$ is the interference term between chains. In equation 4, the fraction of hydrogenous polymer is C_H and the fluctuation in scattering power is defined as

$$\delta a_H = (a_H - a_D)(1 - C_H) \qquad (5)$$

The quantity of primary interest is the scattering form factor $f(\mathbf{q})$ for a single chain; this is defined as

$$f(\mathbf{q}) = \sum_{i,j} \exp[i\mathbf{q}(\mathbf{r}_i - \mathbf{r}_j)] \qquad (6)$$

To obtain the scattering due to a single chain in non-dilute conditions, two solutions of the same polymer concentration but with different hydrogen/deuterium ratios are measured. This provides two expressions in the form of equation 4c which may be algebraically combined and

solved for f(**q**). This mixed labelling technique is applicable to a broad range of solution concentrations, as recently demonstrated by Ullman et al.[19,20]

In the case of scattering from dilute solutions of hydrogenous chains in perdeuterated solvents, equation 2 reduces directly to the single chain scattering form factor since α and β are equal (i.e. all the chains are hydrogenous). The single chain scattering form factor is related to the radius of gyration of the polymer chain as shown by Zimm.[21] Since a series approximation is involved, this model is only applicable over the range $qR_g << 1$. When these qualifications are met, the scattering from a dilute polymer solution with concentration C_p is

$$\frac{K'C_p}{I(q)} = \frac{1}{M}\left[1 + \frac{q^2\langle R_g^2\rangle}{3}\right] + 2A_2C_p \qquad (7)$$

In equation 7, M is the weight-average polymer molecular weight and A_2 is the second virial coefficient. The constant K' contains machine parameters and contrast factors. The radius of gyration R_g can be determined from the slope of a linear $C_p/I(q)$ vs. q^2 plot and is independent of normalization and the constant K'. The molecular weight is derived from the intercept and is therefore less accurate due to its dependence on absolute intensity and contrast factors.

If the scattering angle is maintained at a fixed small value and the variation in scattered intensity with concentration is studied, then equation 7 can be written as

$$\frac{K''C_p}{R_\Theta} = \frac{1}{M} + 2A_2C_p \qquad (8)$$

In equation 8, $I(\mathbf{q})$ has been replaced by the Rayleigh ratio R_Θ since this expression is often used for light scattering. The necessary changes in scattering contrast terms are contained in the new constant K" which includes the refractive index of the solvent and the specific refractive index increment. This relation was used to analyze the variation of scattered light intensity as a function of ionomer solution concentration. By plotting the data in this manner, the molecular weight is obtained from the intercept while A_2 is directly related to the slope.

An alternate model for the angular dependence of scattered radiation was derived by Debye with the assumption of a Gaussian random walk for the polymer chain.[22] The resulting relationship is

$$f(\mathbf{q}) = \frac{2}{u^2}[e^u - 1 + u] \qquad (9)$$

where $u=q^2\langle R_g^2\rangle$. The value of R_g can be obtained by fitting the single chain scattering with this functional form and the polymer molecular

weight can be determined from the scattered intensity extrapolated to zero angle.

Quasi-elastic Scattering.

The primary measurement in quasi-elastic light scattering is of the time-correlation function G(t).[23] This function is defined as the correlation between intensity I scattered at times t=0 and t=t.

$$G(t) = \langle I(0)I(t) \rangle \tag{10}$$

for dilute solutions, the electric field correlation function g(t) is obtained as

$$g(t) = \left| \frac{G(t) - A}{A} \right|^{1/2} \tag{11}$$

where A is the measured baseline. For narrow distributions of small scatterers, g(t) decays like a single exponential. In general, however, the time correlation function does not decay single exponentially and so a cumulant fit is commonly performed. This describes the time correlation function at short delay times as

$$\ln(g(t)) = -\Gamma t + \mu_2(\Gamma t)^2/2 + \mu_3(\Gamma t^2)/6 + \ldots \quad (12)$$

In equation 12, $\Gamma = -[d\ln(g(t))/dt]_{t\to 0}$ is the first cumulant and μ_2 and μ_3 are dimensionless quantities which depend on the polydispersity and local flexibility of the polymer. For measurements on large particles in the low-q limit,

$$\frac{\Gamma}{q^2} = D_z(1 + B\langle R_g^2\rangle_z q^2 + \ldots) \quad (13)$$

In this relation, D_z is the z-average translational diffusion coefficient and B is a dimensionless parameter whose magnitude depends on the structure and polydispersity of the sample.

Assuming the Stokes-Einstein relationship, it is possible to calculate the hydrodynamic radius R_H of an equivalent hard sphere. That is;

$$D_0 = \frac{kT}{6\pi\eta_0 R_H} \quad (14)$$

where kT is the thermal energy and η_0 is the solvent viscosity. The infinite dilution diffusion coefficient D_0 was assumed equal to the measured diffusion coefficient in these studies. The resulting value for the hydrodynamic radius contains information about both the structure and polydispersity of the dissolved polymer.

CALCULATED RESULTS AND DISCUSSION

NON-IONIZING SOLVENT

Previous solution viscosity studies[9,10,13,24,25] have revealed several unusual phenomena in dilute and semidilute ionomer solutions. These phenomena are due to the presence of polar ionic groups in the polymer and hence are highly dependent upon solvent polarity. This discussion focuses on sulfonated polystyrene ionomers dissolved in a relatively nonpolar solvent. In such an environment, a majority of the metal counterions remain attached to or in the near vicinity of the sulfonate groups. These metal sulfonate species attempt to escape the nonpolar solvent environment by forming ionic associations. This process is however hindered by the chemical attachment of the sulfonate groups to the hydrocarbon chain.

Ionomers dissolved in these non-ionizing solvents exhibit a dramatic reduction in solution viscosity as the dilute concentration regime is approached. This has previously been interpreted as due to coil collapse. As polymer concentration is increased, the solution viscosity increases dramatically and gelation eventually occurs due to extensive intercoil associations. At an intermediate concentration, the ionomer solution viscosity is the same as that of an equivalent solution

of unmodified polymer. This has previously been explained as a delicate balance between inter- and intra-chain associations.

The determination of an actual molecular basis for these viscometric phenomena is clearly of interest. To this end, a combination of small-angle light scattering (SALS), quasi-elastic light scattering (QELS) and small-angle neutron scattering (SANS) measurements have been performed on this model ionomer system. The solvent of choice was tetrahydrofuran (THF). This non-ionizing solvent (ε=7.6) was used in its perdeuterated form for the SANS studies to reduce incoherent background scattering. The inclusion of known amounts of deuterated chains in the polystyrene ionomers made it possible to measure the radius of gyration of both an associated ionomer aggregate and a single chain within such an aggregate. Measurements were made on materials with a variety of sulfonation levels, molecular weights and counterions and are compared with the unmodified polystyrene precursor results.

Typical solution viscosities for SPS ionomers dissolved in THF are shown in Figure 1. As mentioned above, the reduced viscosity of the ionomer solution at low concentrations is less than that of unmodified polystyrene. It is of interest to focus on this low concentration limit and determine the molecular reasons for the lowered viscosity.

In order to estimate the size of the individual polymer species in solution, the diffusion coefficient D_T was measured by QELS. As

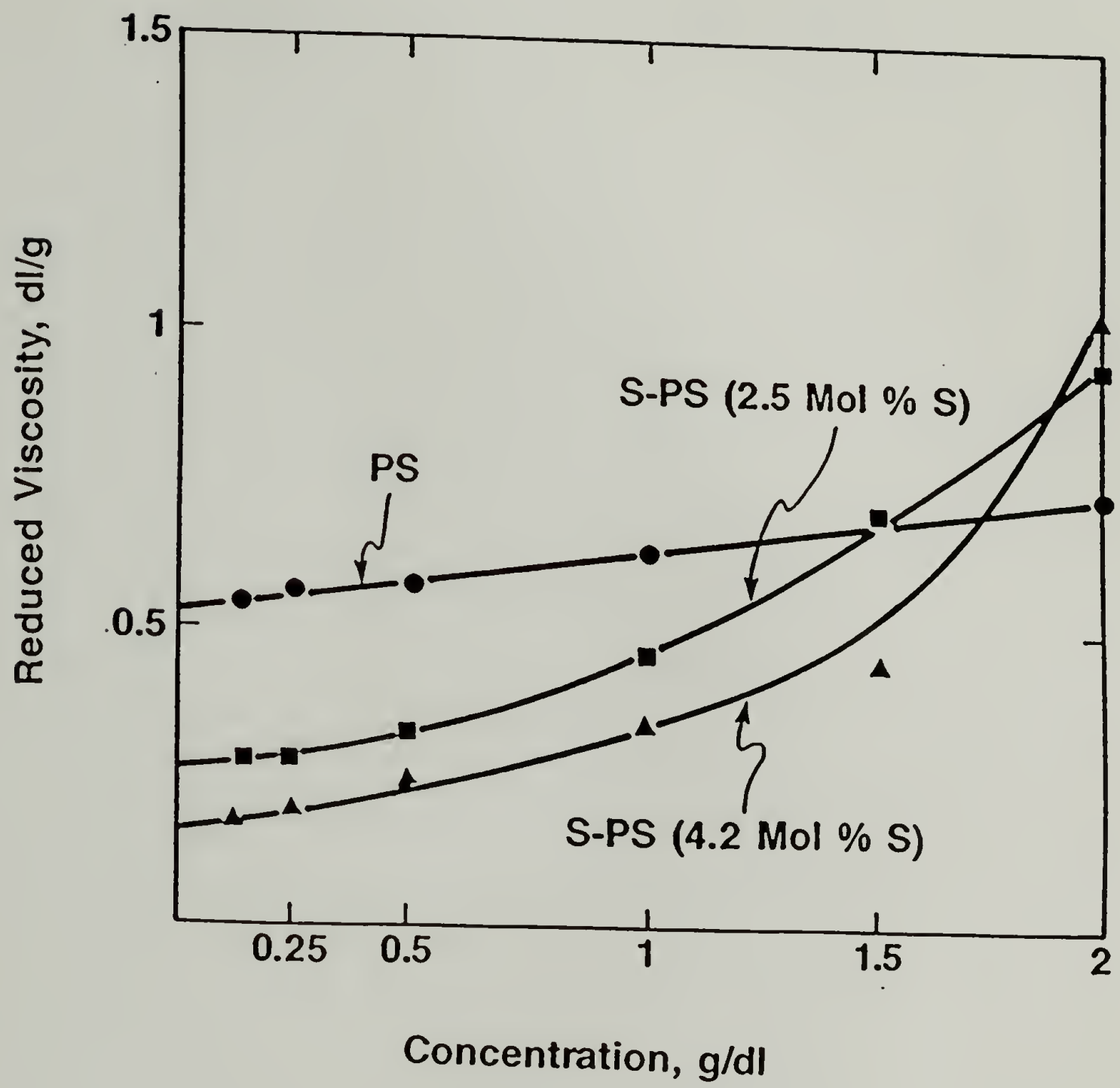

Figure 1. Solution viscosity vs. concentration for Na salts of sulfonated polystyrene (100,000/g mol) dissolved in tetrahydrofuran.

described in a preceding section, the time correlation function was measured and used to calculate the effective diffusion coefficient D_z. Using the Stokes-Einstein relation (equation 14) allows the calculation of an effective hydrodynamic radius for the dissolved species. These results are shown in Figure 2. From the results, it is readily apparent that aggregation occurs at the higher sulfonation levels. This aggregation is evidenced by the several-fold increase in effective size with increasing sulfonate content. It should be noted that the data for the highest sulfonation level of the 1,800,000 g mol^{-1} series is indicative of this trend but is of lower accuracy than the other data points since the aggregated species are too large to filter (see Table 3). Based on the solution viscosity data of Figure 1, aggregation is unexpected at these low concentrations. Its presence implies that the lowering of reduced viscosity is determined by a more complicated balance of inter- and intra-molecular associations than originally postulated.[10]

It is interesting to note that these aggregates can be "broken up" by dilution. This is most clearly seen in the case of 100,000 g mol^{-1} polystyrene with 4.73 mol% sulfonation as shown in Figure 2. The scattering from this solution was measured at concentrations as low as $1x10^{-6}$ g dl^{-1}, the experimental limit of our apparatus. The continuous change in effective hydrodynamic radius below concentrations of $1x10^{-5}$ g dl^{-1} is evidence of the dynamic nature of the aggregation process. At

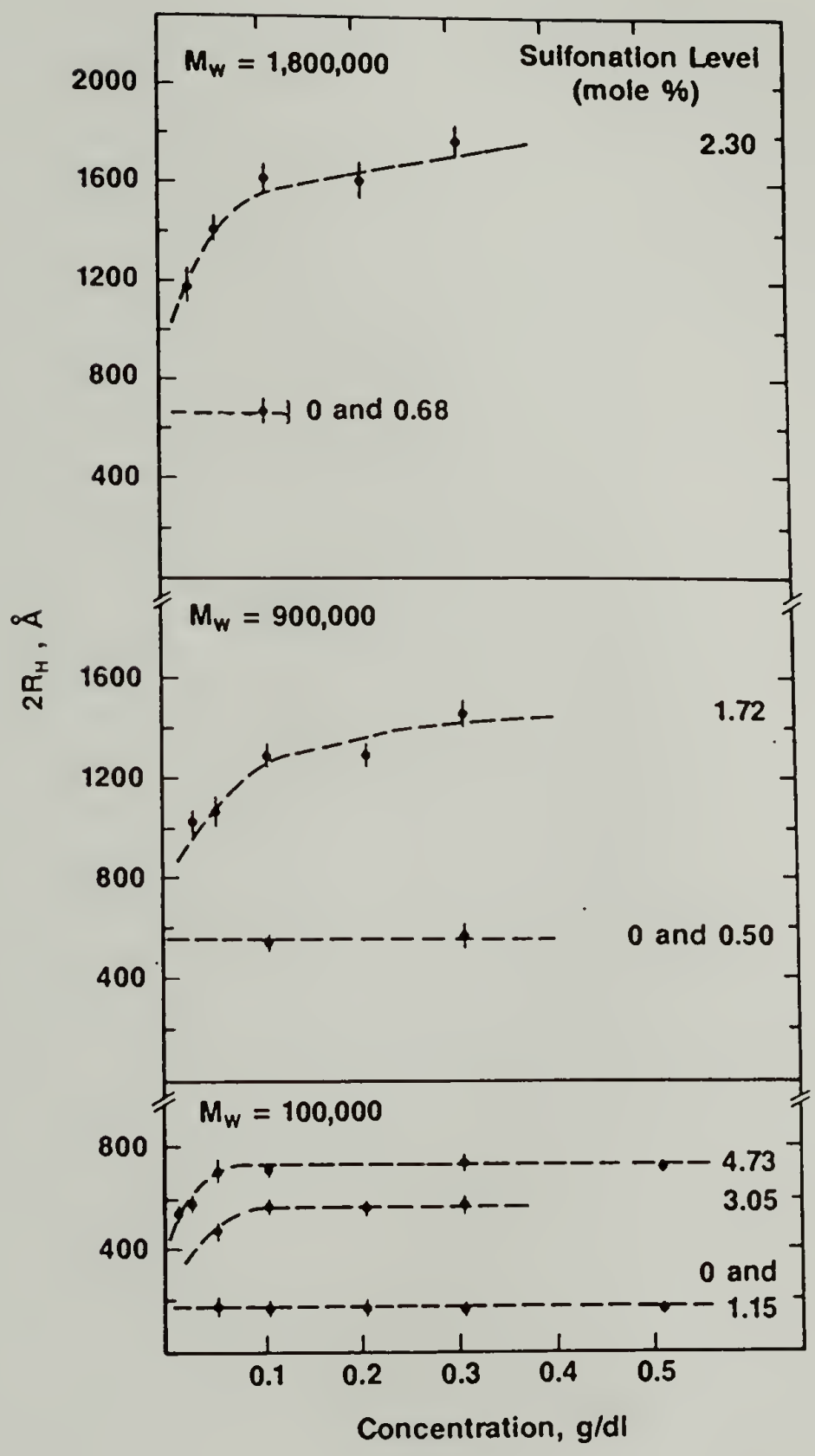

Figure 2. Quasi-elastic light scattering data for Na salts of sulfonated polystyrene dissolved in tetrahydrofuran.

lower concentrations, less aggregation occurs. Similar trends are seen in the 900,000 and 1,800,000 g mol^{-1} series as well.

Having determined that the effective size of these aggregates is relatively constant throughout the limited concentration range of 0.1 to 0.5 g dl^{-1}, it is now possible to determine the quality of solution as measured by SALS. Typical results from this series of lightly sulfonated polystyrenes dissolved in THF are shown in Figure 3 and Table 3. The ionomer results are directly compared with those of the unmodified polystyrene precursor. The data are presented as $K"C_p/R_\theta$ versus polymer concentration as explained in the preceding section.

A close examination of Figure 3 shows that the second virial coefficient of the solution is rapidly reduced as the level of sulfonation is increased. This decrease in the value of A_2 corresponds to a decrease in solution quality. Theta conditions (where $A_2 = 0$) are approached at very low sulfonation levels. In general, the higher the molecular weight, the lower the charge density required to approach theta conditions. This effect can also be seen in Table 3. where the higher molecular weight materials are soluble over a more limited range of sulfonation levels. The measured decrease in second virial coefficient with increasing ionic content is consistent with recent theoretical predictions of Cates and Witten.[26] Conditions similar to those found for ordinary chains near the Flory theta temperature have been predicted for idealized materials where the number of monomers

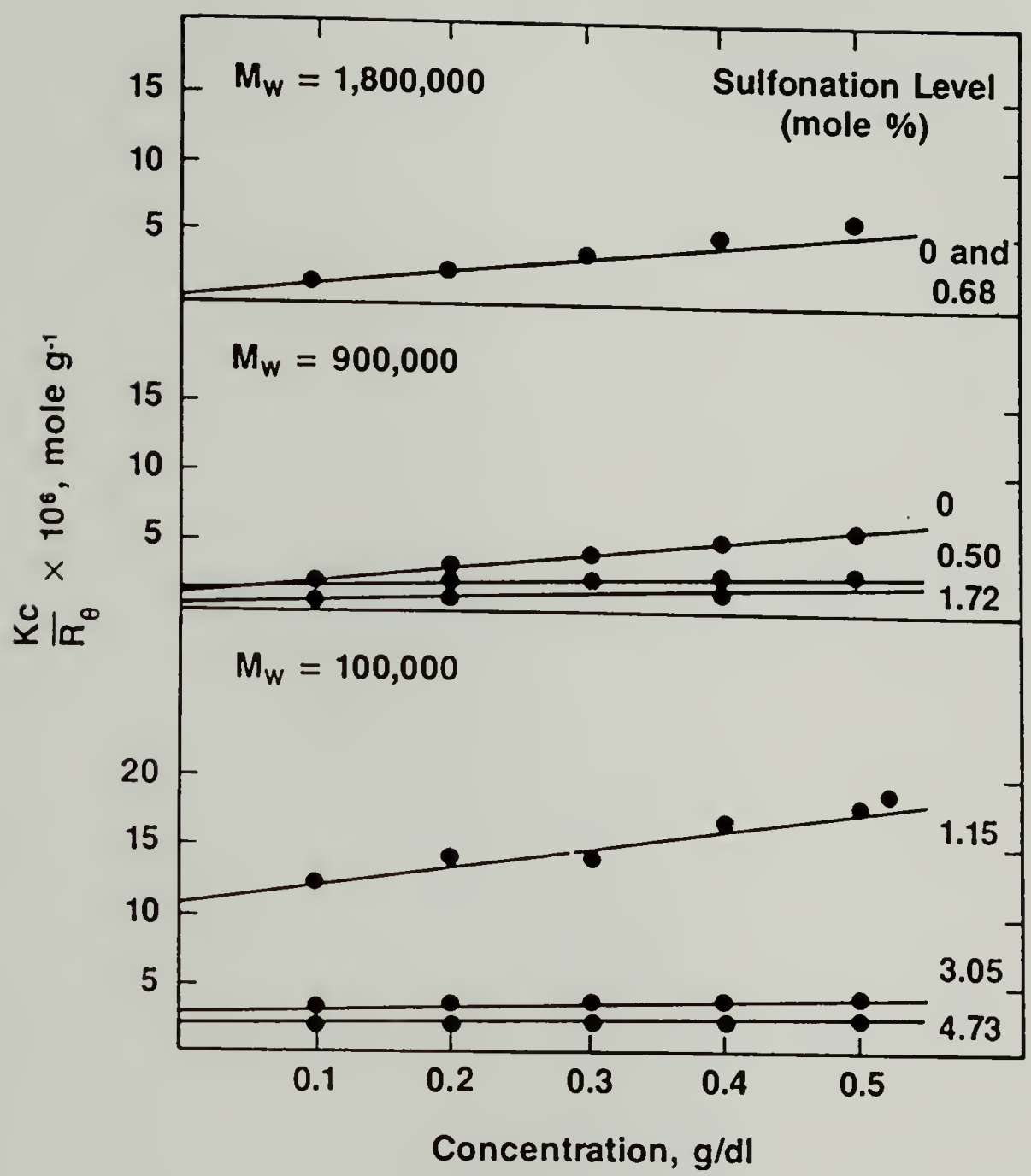

Figure 3. Static small-angle light scattering data for Na salts of sulfonated polystyrene dissolved in tetrahydrofuran.

Table 3. Static Light Scattering Results for Na-SPS in THF.

Molecular Weight (g/mol)	Sulfonation Level (mol%S)	Measured Molecular Weight (g/mol)	$A_2 \times 10^6$ (dl mol g^{-2})
100,000	1.15	91,000 ± 9,000	6.5 ±.7
100,000	3.05	284,000 ± 28,000	0.0 ±.7
100,000	4.73	543,000 ± 54,000	0.7 ±.7
900,000	0	1,023,000 ±100,000	5.0 ±.4
900,000	1.72	5,208,000 ±520,000	3.2 ±.4
900,000	3.20	insoluble	-
1,800,000	0	2,000,000 ±200,000	5.0 ±.4
1,800,000	0.68	2,000,000 ±200,000	5.0 ±.4
1,800,000	2.30	bluish, unfilterable	-
1,800,000	3.80	insoluble	-

between associating groups is large and the associating interaction is both local and very strong. A wider range of molecular weights and ionic contents must be studied to evaluate the scaling predictions of this model. In the present study, the molecular weight of the scattering entity increases with increasing sulfonation level. It should be noted that the data for the highest molecular weight materials in Figures 2 and 3 appear to be insensitive to very low levels of sulfonation. This is probably erroneous and caused by the filtering process. By filtering the solution, the larger aggregates are artificially removed. In the lower molecular weight series, these aggregates are able to pass through the filter and are therefore manifest in the scattering measurements. This aggregation phenomenon is apparently due to the inability of the metal sulfonate groups to interact in a purely intra-molecular manner. As a result, a small number interact intermolecularly. At sufficiently high sulfonation levels, these intermolecular associations lead to insolubility.

The values of A_2 obtained from static low-angle light scattering are presented in Table 3. The second virial coefficient has previously been measured[27] for unmodified polystyrene dissolved in THF and is in reasonable agreement with the values determined in this study. In addition, calculation of $K"C_p/R_\theta$ requires the measurement of the specific refractive index increment, dn/dc. This quantity was measured for a number of the ionomer solutions and the results are compiled in Table 4.

Table 4. Refractive Index Increments for SPS Ionomers.

Molecular Weight (g/mol)	Sulfonation Level (mol%S)	Solvent	dn/dc (ml/g)
1,800,000	0	THF	0.20 ± 0.01
900,000	1.72	THF	0.20 ± 0.01
900,000	1.72	DMF	0.15 ± 0.01

Table 5. Variation of SPS/THF Solution Properties with Counterion.

Molecular Weight = 115,000 g/mol; Sulfonation = 2.49 mol%

Counterion	Measured Molecular Weight (g/mol)	$A_2 \times 10^6$ (dl mol g^{-2})	$D_T \times 10^7$ ($cm^2 s^{-1}$)
Na	190,000 ± 19,000	2.2 ± .7	5.4 ± .2
Zn	116,000 ± 12,000	0.0 ± .7	4.7 ± .2
H	123,000 ± 12,000	7.3 ± .7	5.6 ± .2

An additional aspect of this study of lightly sulfonated polystyrene ionomers in a non-ionizing solvent is the variation of solution properties with counterion. Hara and coworkers[28] have correlated the degree of aggregation with counterion binding for a series of monovalent salts. The effects of counterion valency are considered here. To this end, the static and quasi-elastic scattering from the sulfonic acid and its sodium and zinc salt forms are compared at a fixed molecular weight of 115,000 g mol^{-1}. The variation in static scattering is shown in Figure 4 and the results are given in Table 5. As observed earlier, the sodium salt has a lower value of A_2 indicating poorer solution quality compared to unmodified polystyrene dissolved in THF. This effect is even more dramatic in the case of the zinc neutralized ionomer. Neither of the salt forms nor the free acid is significantly aggregated in solution at this level of sulfonation. This is shown by the molecular weight measured via SALS and by the effective hydrodynamic radius determined from QELS.

Further study of this ionomer system was undertaken in the form of small-angle neutron scattering. Solutions of lightly sulfonated polystyrene sodium salts with 0 and 19% perdeuterated chains were studied throughout a concentration range of 0.5 to 4.0 g dl^{-1} in perdeuterated tetrahydrofuran [THF(D6)]. A 0.5 g dl^{-1} solution of unmodified polystyrene (PS) was also measured for comparison. The hydrogenous polymer had a number-average molecular weight of 100,000 g

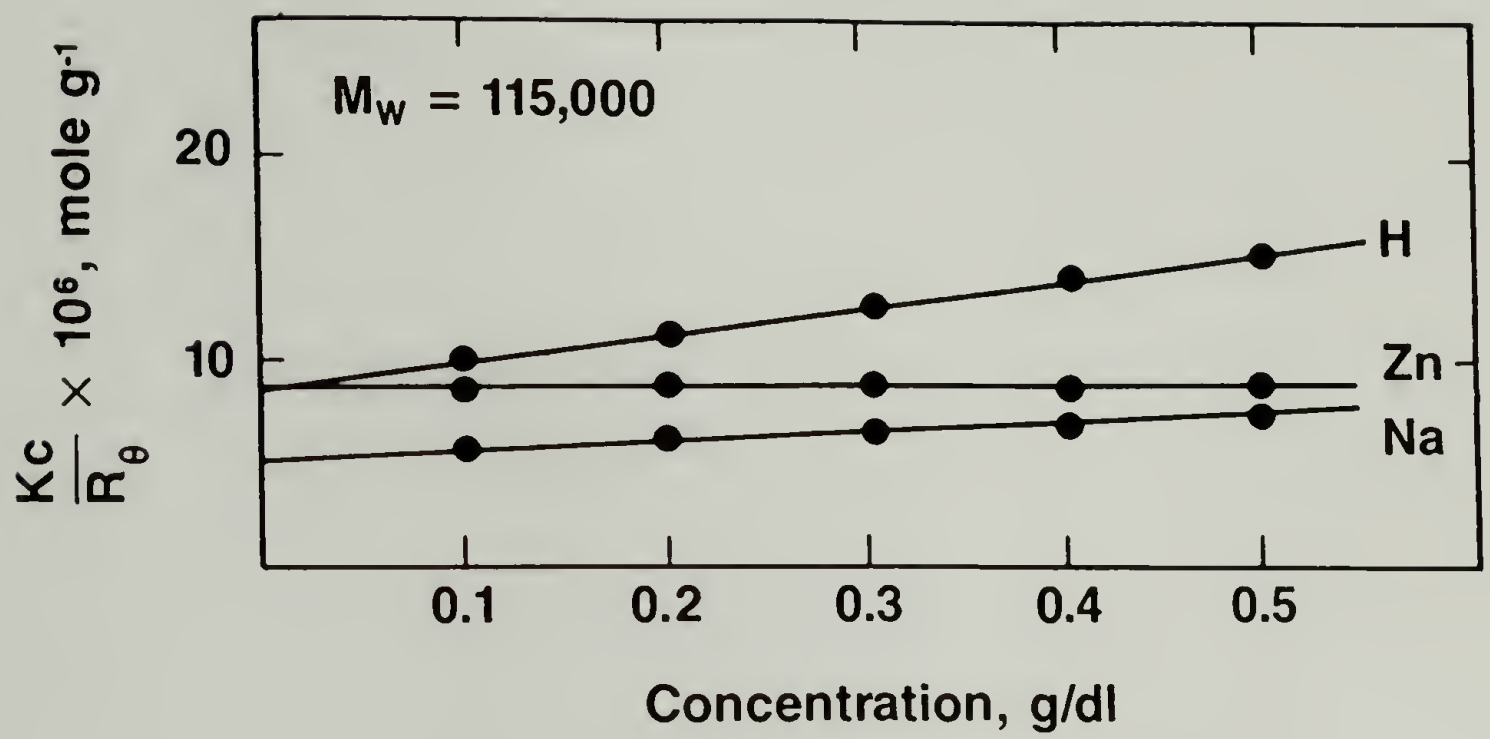

Figure 4. Static small-angle light scattering data for sulfonated polystyrene (2.49 mol%S) dissolved in tetrahydrofuran.

mol^{-1}; this was matched by 104,000 g mol^{-1} for the perdeuterated material.

The scattering from the solution of fully hydrogenous PS in THF(D6) was used to scale the scattered intensity to absolute values. In order to determine molecular weight, corrections must be made for the effects of the second virial coefficient A_2 in equation 7. The literature value[27] of $A_2 = 5.5 \times 10^{-4}$ cm^3 mol g^{-2} was used for the PS/THF(D6) solutions. The second virial coefficient for SPS/THF solutions has been shown to be zero under these conditons and so no correction was necessary for the ionomer solutions.

The scattering from fully hydrogenous SPS in THF(D6) over a range of concentrations is shown in Figure 5. The presence of associations larger than single chains is immediately evident from the dramatic upturn in intensity at low angles. When equation 7 is used to analyze the scattering, the plots shown in Figure 6 are obtained. The resulting values of radius of gyration and molecular weight are listed in Table 6.

The molecular weight values listed in Table 6 indicate that interchain association is present even at concentrations as low as 0.5 g dl^{-1}. As concentration is increased to 4.0 g dl^{-1}, the weight-average number of chains per aggregate rises from three to twelve. It is important to emphasize that this is an average degree of aggregation. Though the individual ionomer chains make up a nearly monodisperse

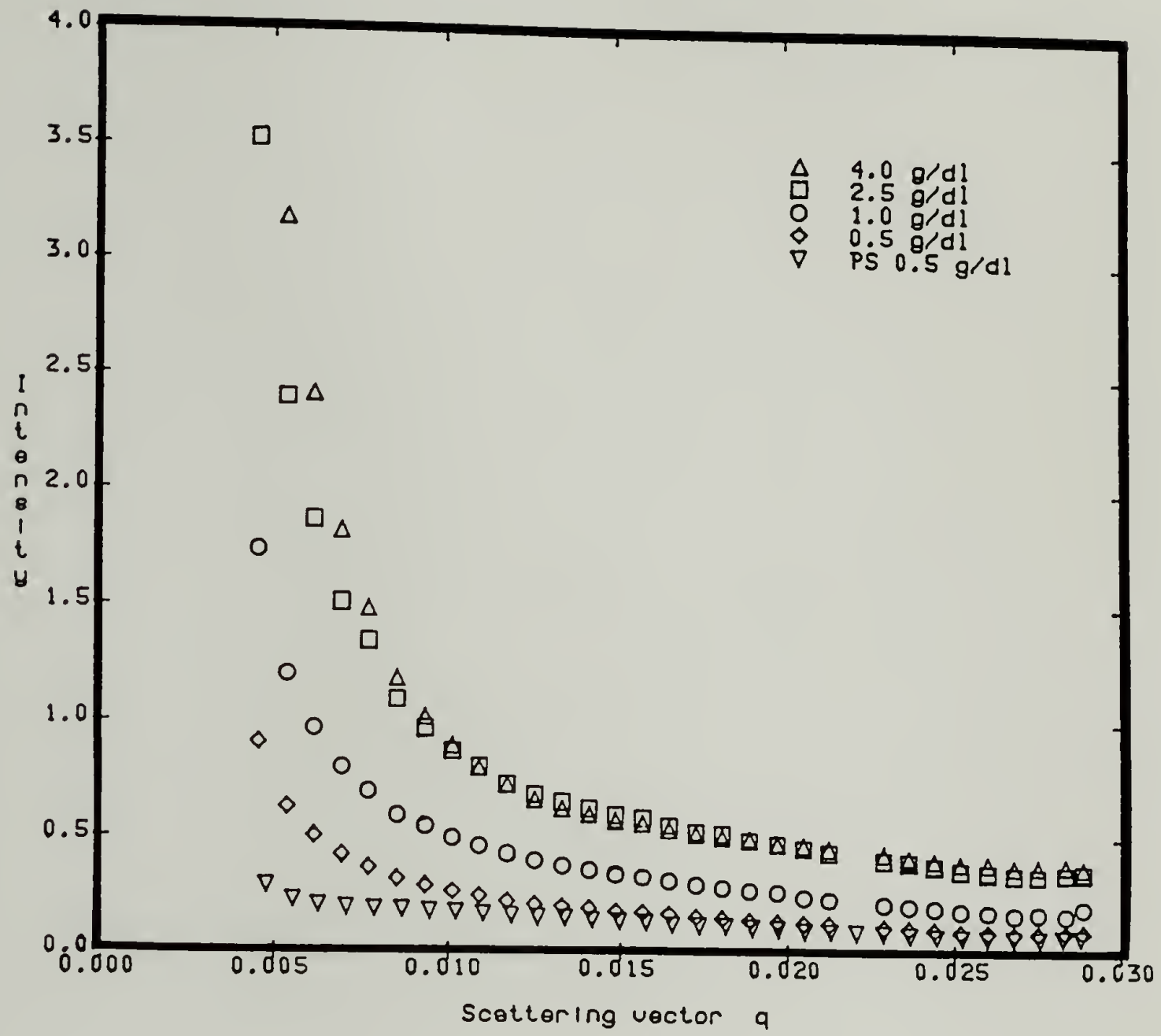

Figure 5. Small-angle neutron scattering data for Na salts of hydrogenous sulfonated polystyrene (100,000 g/mol ; 4.2 mol%S) dissolved in perdeuterated tetrahydrofuran.

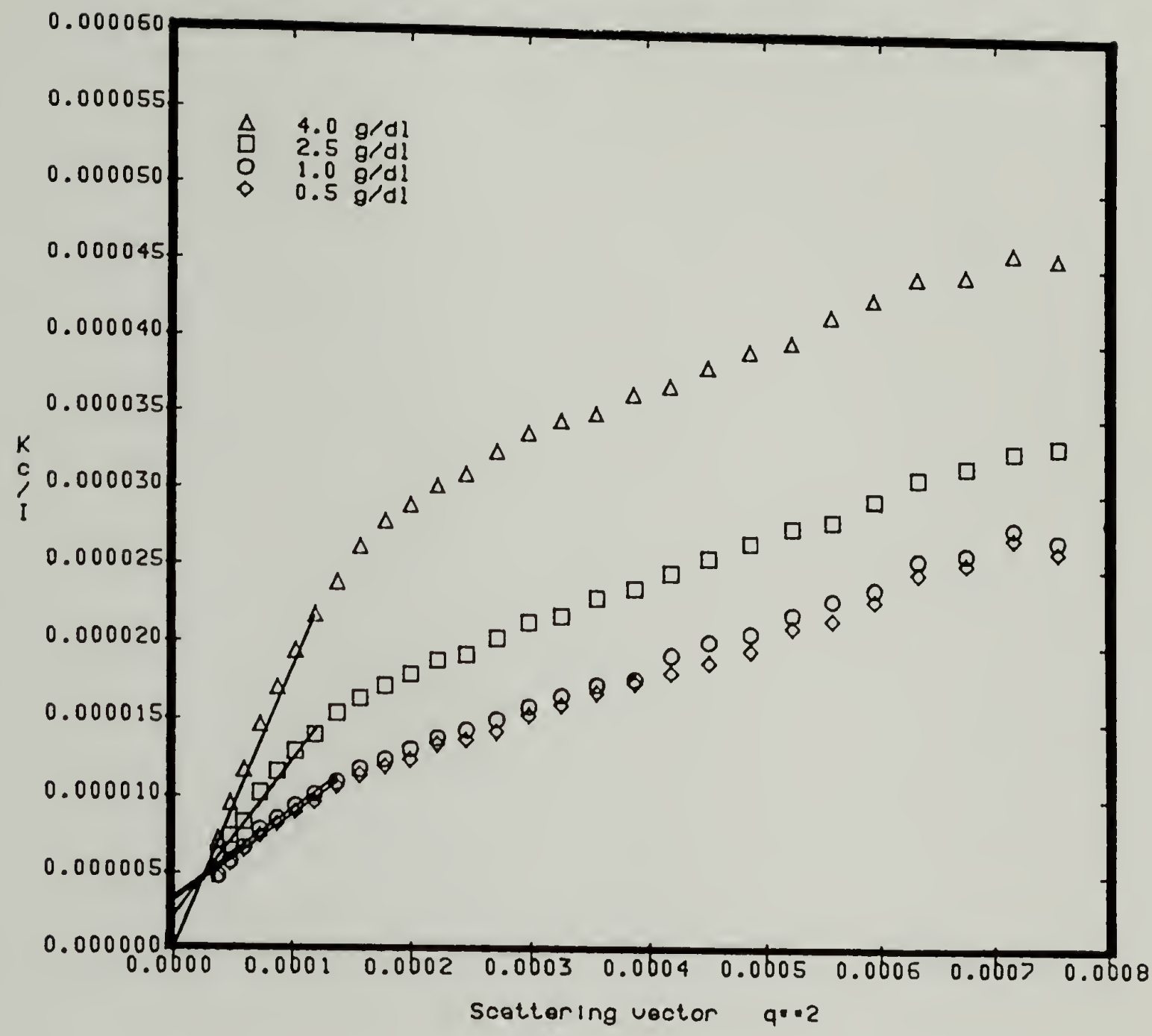

Figure 6. Zimm analysis of the data in Figure 5.

Table 6. Aggregate Parameters for SPS/THF solutions determined by SANS.

System	Concentration (g/dl)	Radius of Gyration (A)	Molecular Weight (g/mol)
SPS 100,000 (4.2 mol%S)	4.0	790 ± 120	1,164,000±233,000
	2.5	390 ± 40	471,000 ±71,000
	1.0	226 ± 23	299,000 ±45,000
	0.5	230 ± 23	317,000 ±48,000
PS 100,000	0.5	134 ± 13	assumed 100,000

Table 7. Single Chain Parameters for SPS/THF solutions from SANS.

System	Concentration (g/dl)	Radius of Gyration (A)	Molecular Weight (g/mol)
SPS 100,000 (4.2 mol%S)	4.0	104 ± 10	135,000 ±20,000
	2.5	124 ± 12	190,000 ±29,000
	1.0	110 ± 11	184,000 ±28,000
	0.5	128 ± 13	--------
PS 100,000	0.5	113 ± 11	104,000 ±15,000

ensemble, there is no reason to anticipate a narrow distribution of aggregate sizes. In fact, the strong downward curvature present in the plots of Figure 6 is consistent with a polydispersity greater than two.[29,30] For this reason, only the initial portions of the $K'C_p/I(q)$ versus q^2 plots can be used.

Concomitant with the increase in molecular weight, the radius of gyration of an aggregate increases with concentration. These values also appear in Table 6. At the lowest concentration of this study, the results may be compared with the previous light scattering measurements. Although the identical system was not studied, it is possible to interpolate the light scattering results and predict an approximate hydrodynamic radius of 380Å and an approximate average aggregate molecular weight of 400,000 g mol^{-1}. These values are in reasonable agreement with the SANS measurements.

These results are a bit startling when first compared with the solution viscosity measurements shown in Figure 1. The reduced viscosity at 0.5 g dl^{-1} is markedly higher for PS than for its sulfonated analog and yet PS has a smaller radius than the sulfonated aggregate. Actually, the solution viscosity of an unassociated solution can be greater than that of an aggregated system if the density of material within a viscometric particle changes.

For example, if the well known Flory relation[31] is assumed and the intrinsic and reduced viscosities are considered comparable at low concentrations, then the solution viscosity may be roughly approximated by

$$\eta_{red} = \frac{\kappa(R_g)^{3/2}}{M} \qquad (15)$$

If the data for PS shown in Figure 3 are now used to calculate the proportionality constant κ and the measured radii of gyration and molecular weights of SPS at the two lowest concentrations are inserted in equation 15, then a reduction of up to 40% in η_{red} is predicted for the SPS solutions. Clearly, this naive calculation cannot be expected to predict solution viscosity precisely but its implication is nonetheless of great importance: the presence of aggregation at low SPS concentrations in THF is not inconsistent with the solution viscosity measurements.

It now remains to determine the dimensions of a single ionomer chain within an associated aggregate. To obtain this information, the mixed labelling technique described previously was used. This subtraction technique was tested on solutions of unsulfonated polystyrene. The scattering from a 0.5 g dl^{-1} solution of 19% perdeuterated PS in THF(D6) was measured and the results were combined with those of the fully hydrogenous polymer to calculate the single chain scattering form factor f(q). Since the solution is dilute for PS

at this concentration and molecular weight, the subtraction technique should yield the same results as the fully hydrogenous chains. The resulting values appear in Table 7. As can be seen by comparing Tables 6 and 7, the two measurements agree within experimental error and the correct molecular weight is measured by the subtraction technique.

Solutions of SPS containing 19% perdeuterated chains were measured at the same concentrations as the completely hydrogenous ionomers. The results were combined to yield single chain information. An example of this combination is shown in Figure 7. The resulting single chain scattering patterns are shown in Figure 8. As with the overall scattering from the aggregates, equation 7 was used to determine the radius of gyration and molecular weight of the single chain. The appropriate plots are shown in Figure 9.

The molecular weight of a single chain should, of course, be constant with variation in concentration. As can be seen in Table 7, the molecular weights are indeed constant within experimental error. The values are somewhat greater than expected, reflecting the uncertainty in determining absolute scattering intensity.

It is important to note that the radius of gyration of a single ionomer chain also remains constant within experimental error as concentration increases. There is no evidence for significant coil collapse throughout the concentration range studied. Presumably, coil

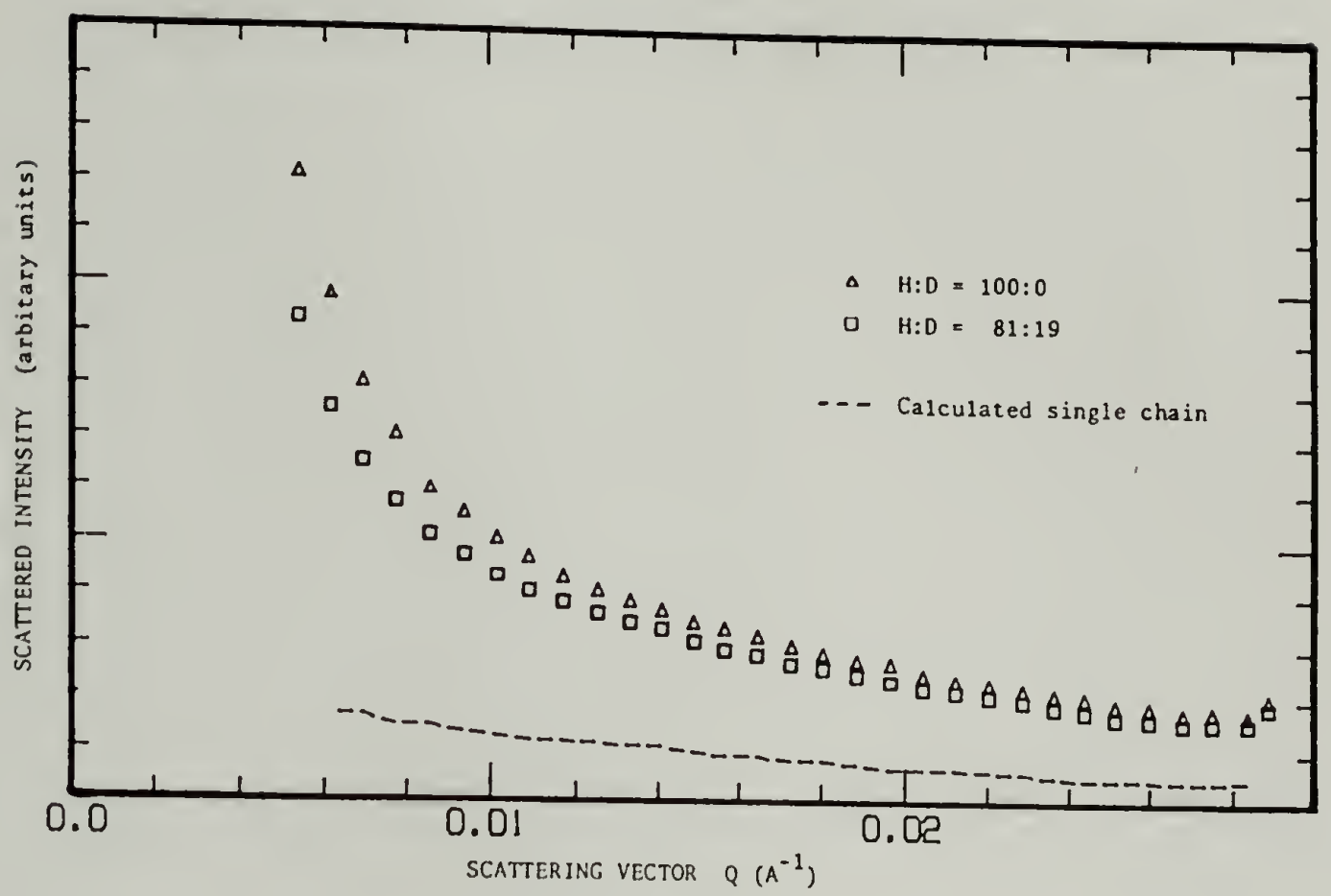

Figure 7. Mixed labelling subtraction technique in tetrahydrofuran.

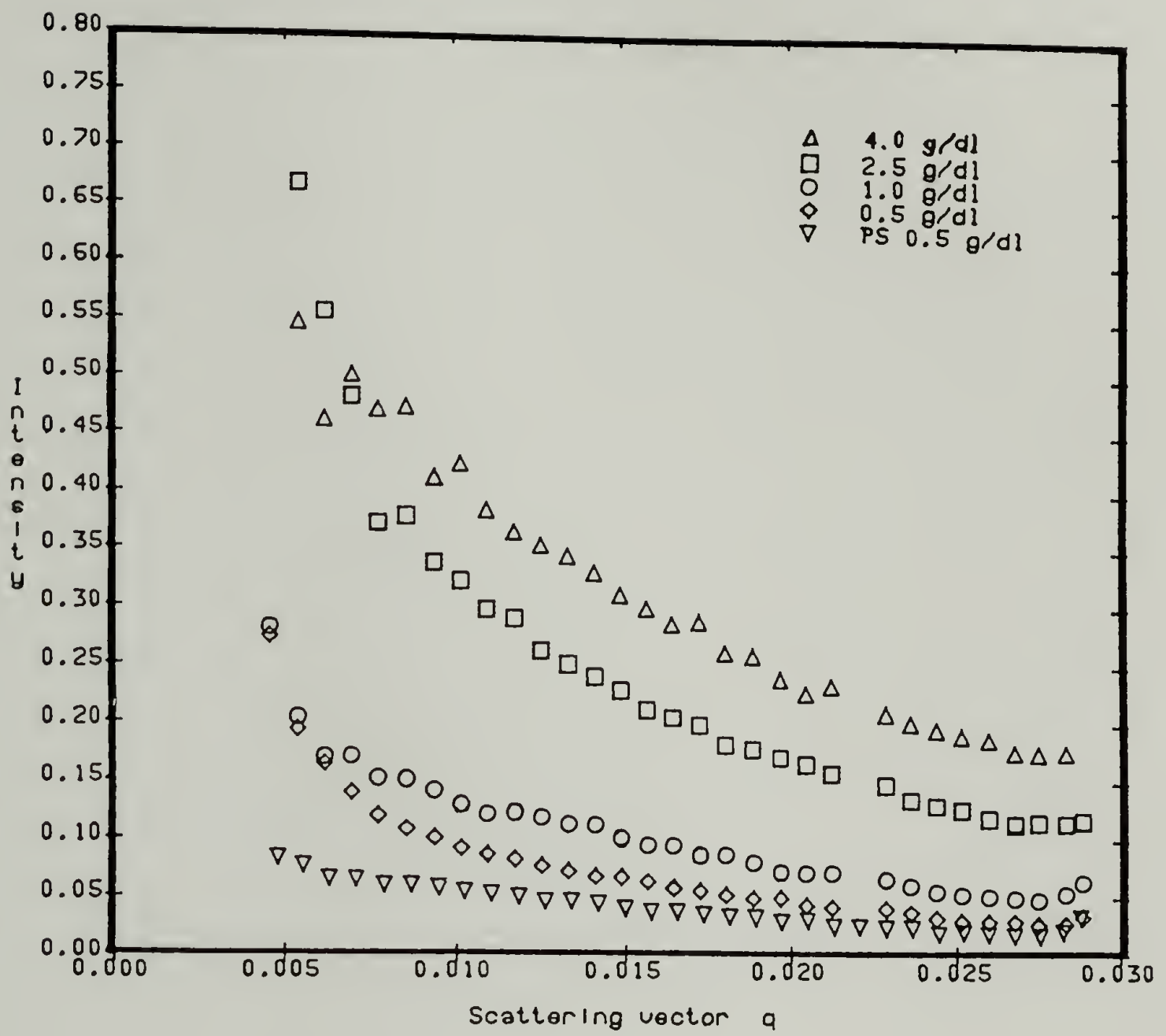

Figure 8. Calculated single chain scattering for Na salts of sulfonated polystyrene (100,000 g/mol; 4.2 mol%S) dissolved in perdeuterated tetrahydrofuran.

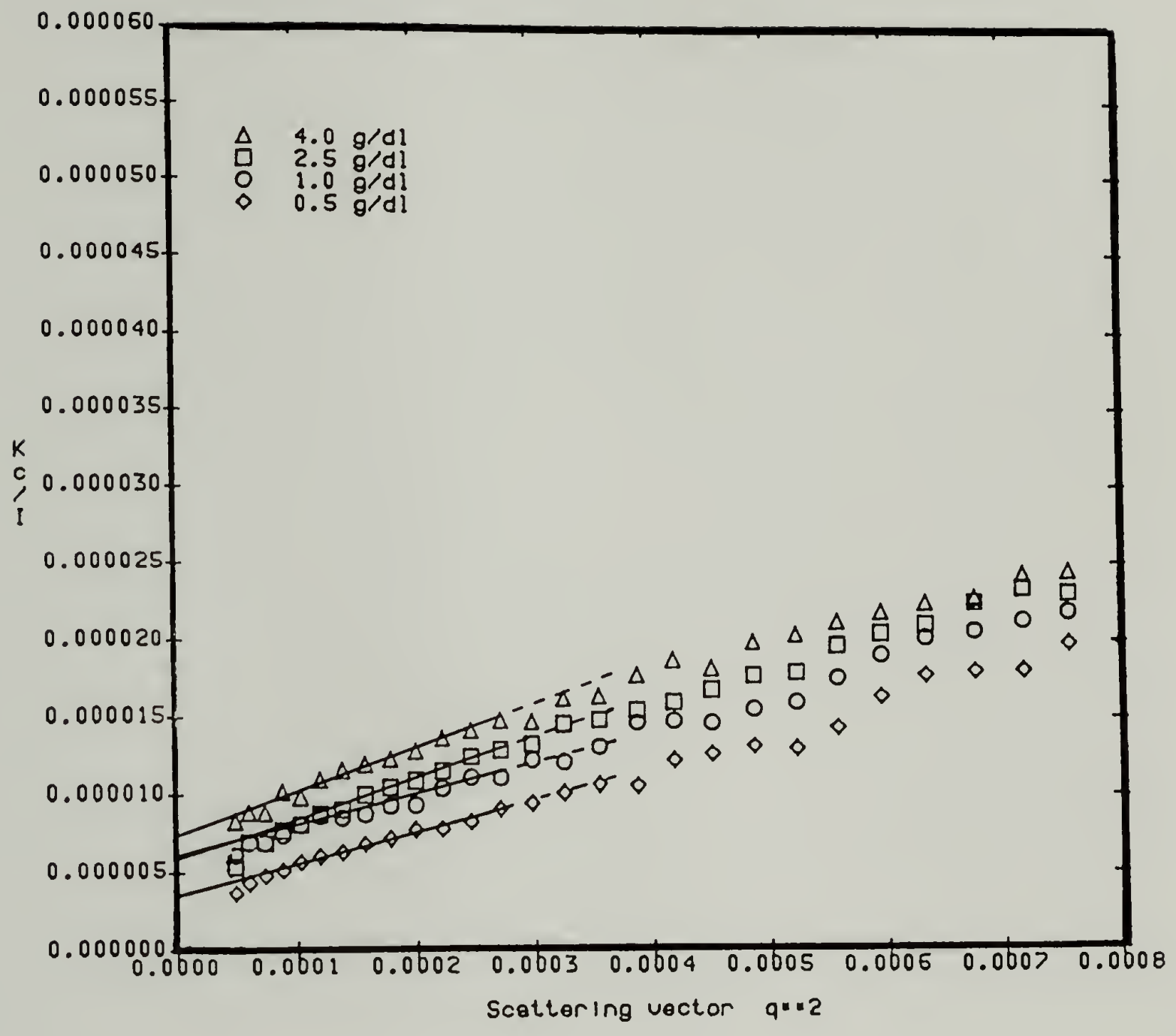

Figure 9. Zimm analysis of the data in Figure 8.

collapse might be seen at even lower concentrations where light scattering studies suggest that these aggregates dissociate and intra-chain associations should dominate. Significantly, there is no evidence for single coil expansion either as concentration is increased. The resulting picture of ionomer solutions, schematically shown in Figure 10, is one where single coils associate into aggregates without significant changes in individual size. Interestingly, the radius of gyration of a single ionomer chain within such an aggregate is very comparable to dimensions measured in the bulk.[32]

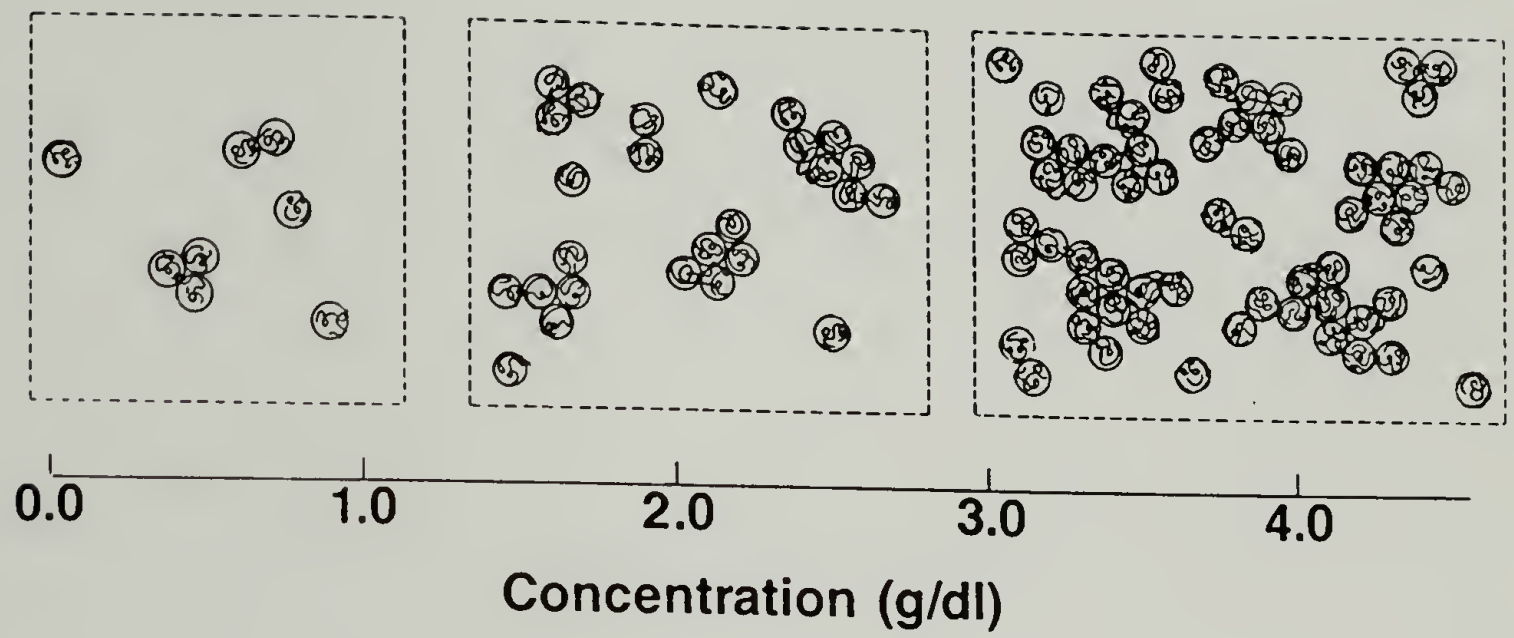

Figure 10. Schematic of an ionomer dissolved in a non-ionizing solvent.

IONIZING SOLVENTS

Solutions of charged macromolecules may exhibit a wide variety of properties depending on the solvent quality and polarity and the charge density of the solute. One particularly interesting case is ionomer solutions. Ionomers such as lightly sulfonated polystyrene contain ionic groups which interact strongly with one another in a manner which is highly dependent on the choice of solvent. This discussion focuses on sulfonated polystyrene ionomers dissolved in an ionizing solvent.

In solvents of high polarity, ionomers exhibit solution viscosity behavior which is reminiscent of classical polyelectrolytes. That is, a marked upsweep in reduced viscosity is observed as polymer concentration is decreased. It is rather novel that materials of such low ionic content can display this characteristic polyelectrolyte effect. The molecular basis for classical polyelectrolyte solution behavior remains an elusive unknown. To establish such a basis for ionomer solutions, a combination of quasi-elastic light scattering (QELS), small-angle light scattering (SALS) and small-angle neutron scattering (SANS) measurements have been performed on a model ionomer system. Specifically, lightly sulfonated polystyrene ionomers of narrow molecular weight distribution have been studied in dimethyl formamide (DMF). This polar solvent (ε=36.1) was used in its perdeuterated form for the SANS measurements to

reduce the incoherent background scattering. By replacing known amounts of the hydrogenous chains with perdeuterated ones, it was also possible to calculate the coherent scattering from a single macromolecule in semi-dilute conditions. Measurements were made on materials with a variety of molecular weights and sulfonation levels and the results are compared with those of the unmodified polystyrene precursor.

Reduced viscosity measurements of lightly sulfonated polystyrene ionomers dissolved in polar solvents have been previously reported[10] for materials of broad molecular weight distribution. Dramatic upturns in viscosity at low concentrations are observed which are characteristic of polyelectrolytes. The current study includes similar measurements on materials of narrow molecular weight distribution. The reduced viscosity measurements for sodium salts of SPS dissolved in DMF are shown in Figures 11 and 12. The characteristic polyelectrolyte effect is seen in these materials as it was with the polydisperse materials. Presumably, this upsweep in reduced viscosity is due to an expansion of the ionomer chain. In this highly polar non-aqueous medium, a sufficient number of salt groups must be ionized to cause an increase in the hydrodynamic volume (and hence in the viscosity) due to repulsion of like charges. As expected, this polyelectrolyte effect is proportional to sulfonation level at a constant molecular weight and the effect increases with molecular weight at a constant sulfonation level.

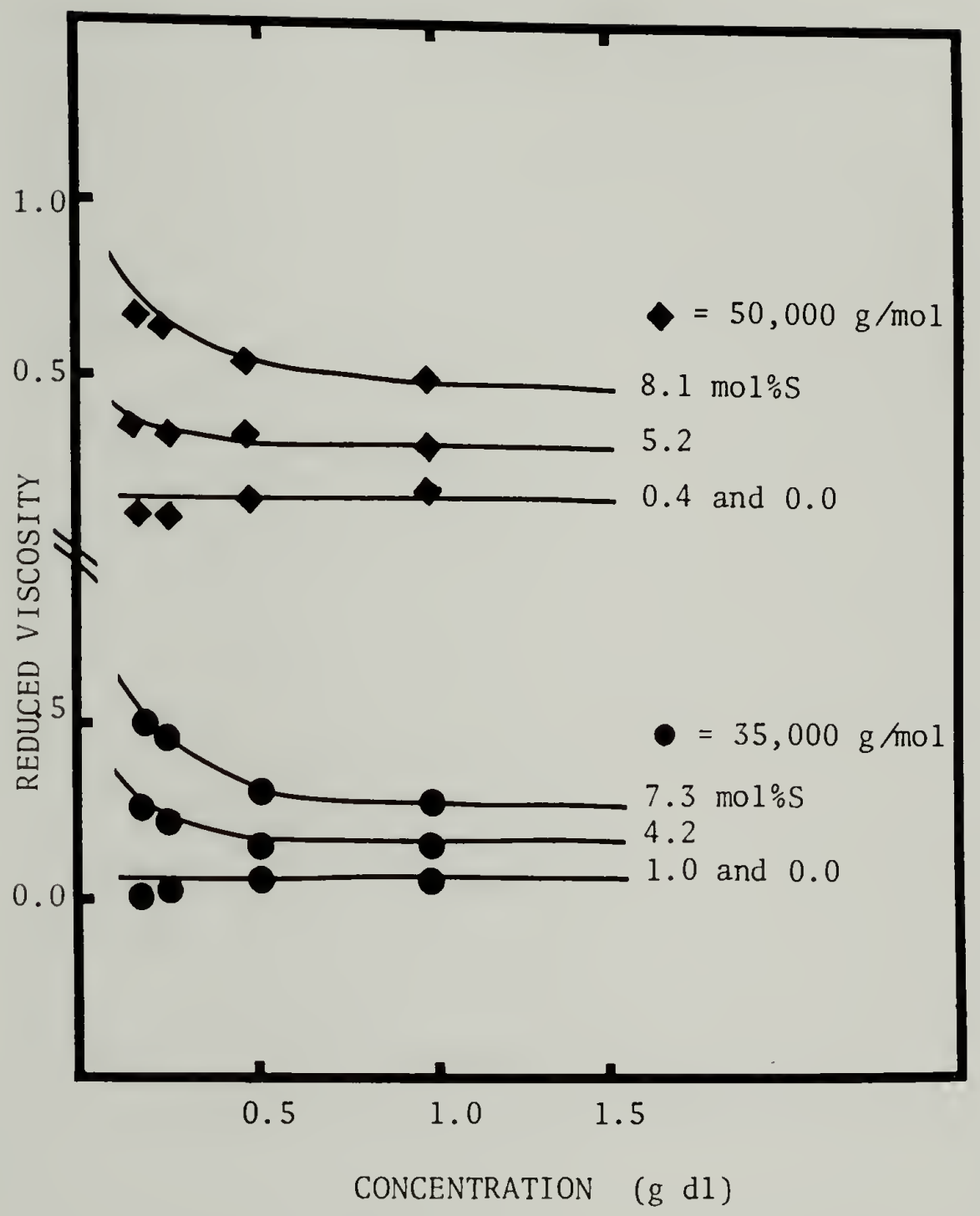

Figure 11. Solution viscosity vs. concentration for Na salts of sulfonated polystyrene dissolved in dimethyl formamide.

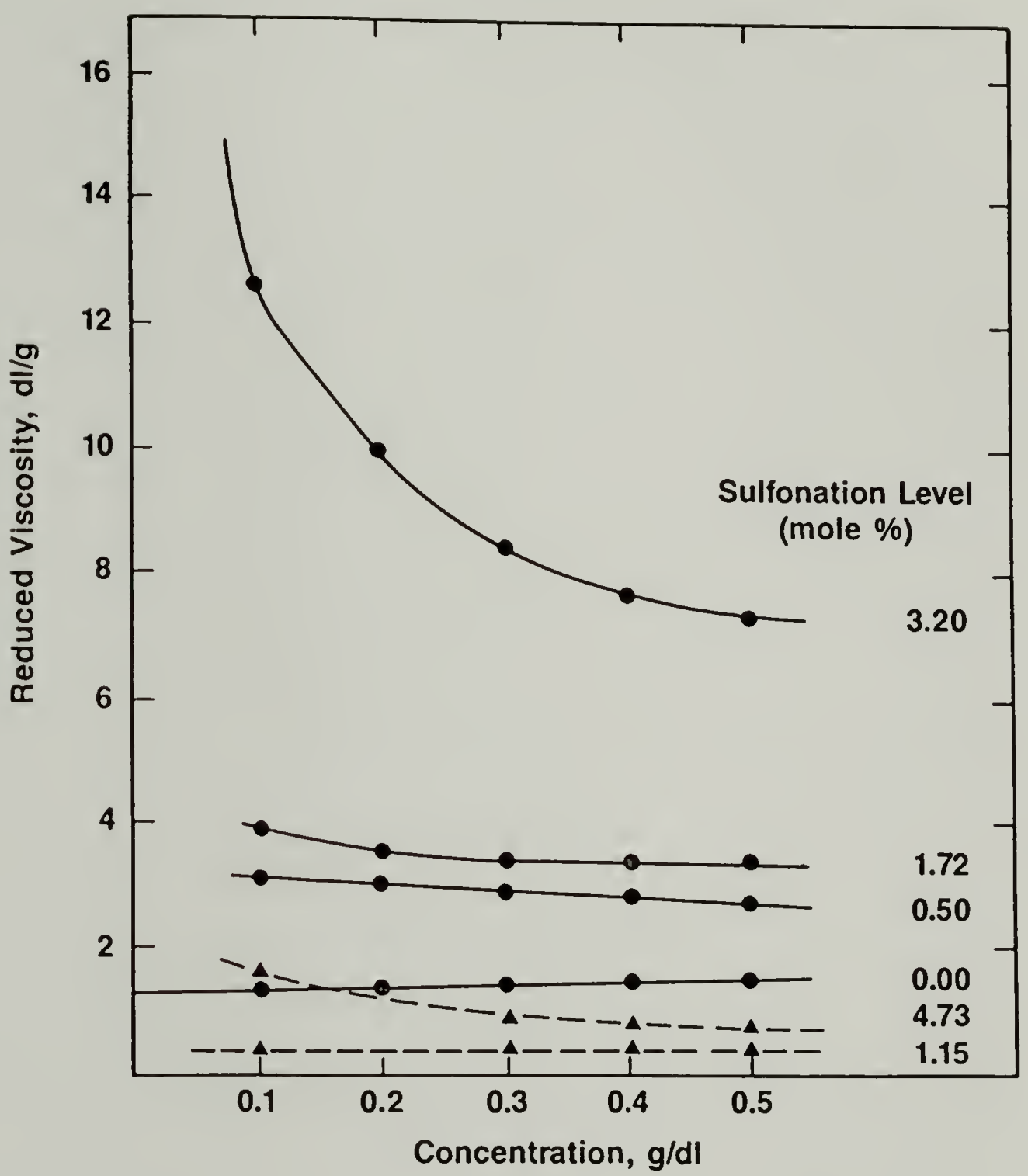

Figure 12. Solution viscosity vs. concentration for Na salts of sulfonated polystyrene (-●- = 900,000 g/mol; -▲- = 100,000 g/mol) dissolved in dimethyl formamide.

The diffusion coefficient D_T of the polymer species in these solutions was measured by QELS. The results, shown in Figure 13, suggest that the diffusion coefficient remains invariant over the concentration range measured. An important consideration in the interpretation of the quasielastic scattering data is whether or not the measured diffusion coefficient may be ascribed to free diffusion of the polymer coils. Equivalently, it must be considered whether or not the solution is dilute. If the solution has a concentration greater than the overlap concentration C^*, then free diffusion of the polymer chain is no longer possible. Rather, it is the motion of a characteristic section ξ of the overlapping polymers which determines D_T. One complication is the calculation of C^* itself. Recent theoretical advances have been made in estimating C^* for polyelectrolyte solutions in the absence of added low molar mass electrolyte.[33-35] However it is not yet possible to decide where the transition from dilute to semi-dilute really lies.

If the Stokes-Einstein relation (equation 14) is used to interpret the diffusion coefficients shown in Figure 13, then an effective hydrodynamic radius can be calculated for these solutions. It should be noted that the use of the Stokes-Einstein equation is questionable for solutions displaying polyelectrolyte behavior since the prerequisite condition of a dilute solution may not have been obtained, as discussed above. Using the results of this calculation and assuming a simple spherical model for these ionomers, the hydrodynamic volume swept out by

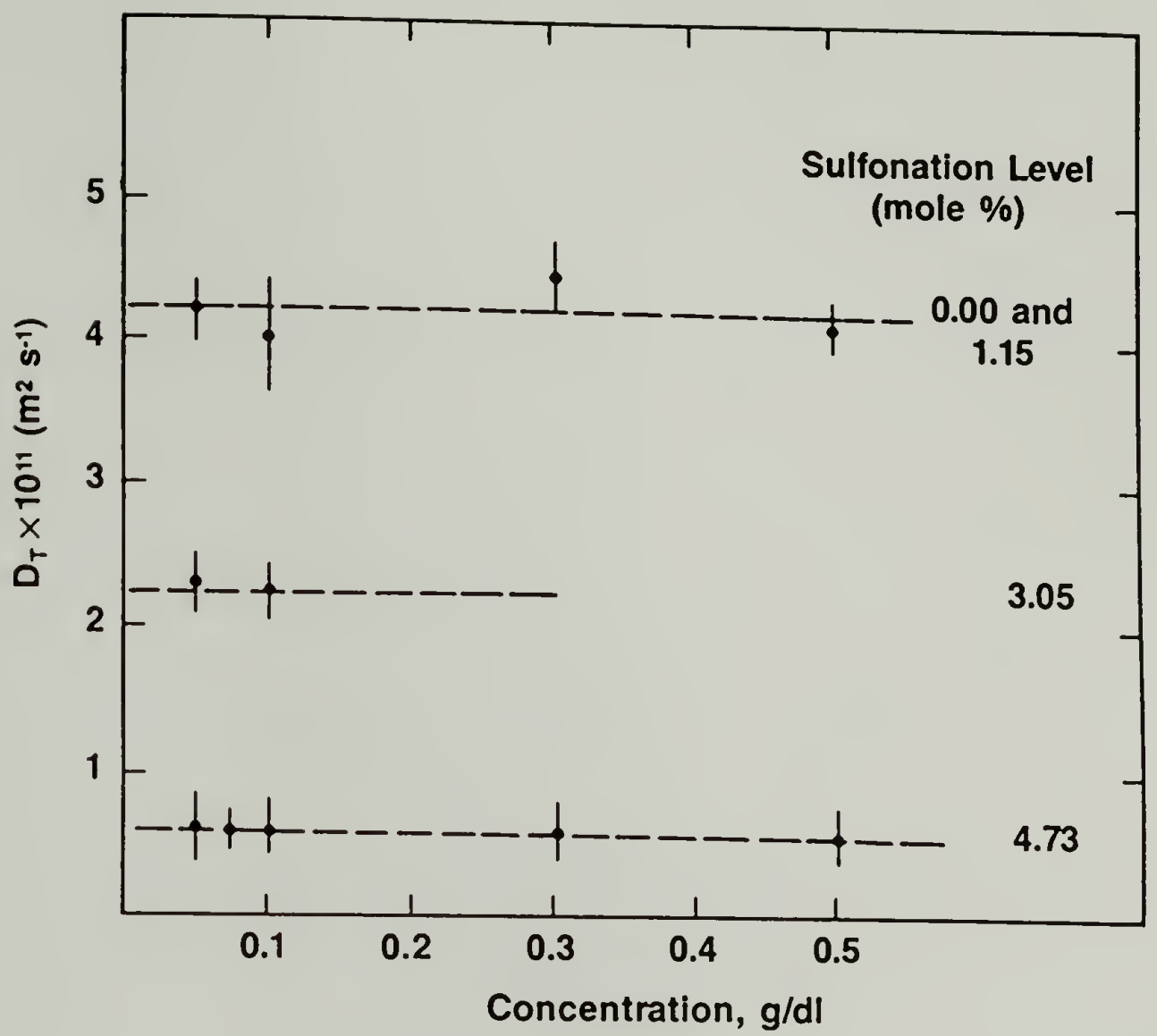

Figure 13. Quasi-elastic light scattering data for Na salts of sulfonated polystyrene (100,000 g/mol) dissolved in dimethyl formamide.

each chain can be calculated. The average volume available to each chain can also be calculated from the concentration. For the chains bearing 0, 1.15, and 3.05 mole percent sulfonation, the spherical hydrodynamic volume is always less than the average volume available to each coil in solution. Therefore it would seem that these solutions are below the overlap concentration and it should be valid to ascribe their diffusion coefficients to free diffusion. In the case of 4.75 mole percent sulfonation however, the volume swept out by the polymer sphere is slightly greater than the average volume available per coil in solution. Nonetheless, a concentration-independent value of D_T is observed indicative of free diffusion. If the concentration is greater than C^*, the question of why a concentration-independent D_T is observed remains. The answer to this apparent contradiction lies in the model chosen for the ionomer chain. The results from SANS indicate that the choice of an independent spherical model is incorrect and that the solutions are, in fact, semi-dilute at these concentrations. Hence the measured D_T should not be attributed to free diffusion. The decrease in diffusion coefficient with increasing sulfonation suggests significant chain expansion. This will be discussed in a following section.

The presence of polyelectrolyte behavior is also manifested in the static SALS measurements. Typical results from a series of sulfonated polystyrenes dissolved in DMF are shown in Figure 14. These results are compared directly with the unfunctionalized polystyrene precursor and are plotted as $K"C_p/R_\Theta$ versus polymer concentration as described in

equation 8. The data in Figure 14 clearly reveal the significant effect of incorporating even a few mole percent of sodium sulfonate groups along the polystyrene chain. Deviations from linearity occur in these plots, even at sulfonation levels as low as 0.50 mol%. Such curvature is indicative of polyelectrolyte behavior[36]. It suggests that considerable chain expansion is present and therefore the resulting scattering is no longer described by the conventional quadratic approximation to the virial equation. As a result, it is not possible to determine a value of A_2 for the ionomer solutions. The second virial coefficient of the PS solutions can be determined however since their $K"C_p/R_\Theta$ vs. C_p plots are linear. The resulting values are given in Table 8.

An additional aspect of this study of lightly sulfonated polystyrene ionomers in DMF is the dependence of solution properties on the nature of the counterion. Hara and coworkers[28,37] have investigated the effect of counterion size for a series of monovalent salts. In the present study, the effects of valency were examined by measuring the static light scattering from the sulfonic acid form and its zinc and sodium salts - each ionomer having a fixed ionic content of 2.49 mol% and a molecular weight of 115,000 g mol^{-1}. The preliminary data are shown in Figure 15 and suggest that the sulfonic acid, zinc and sodium salt each display polyelectrolyte behavior. Presumably, DMF is sufficiently polar to ionize each of these three forms. Chain expansion then occurs due to the resulting charge repulsion. This expansion is

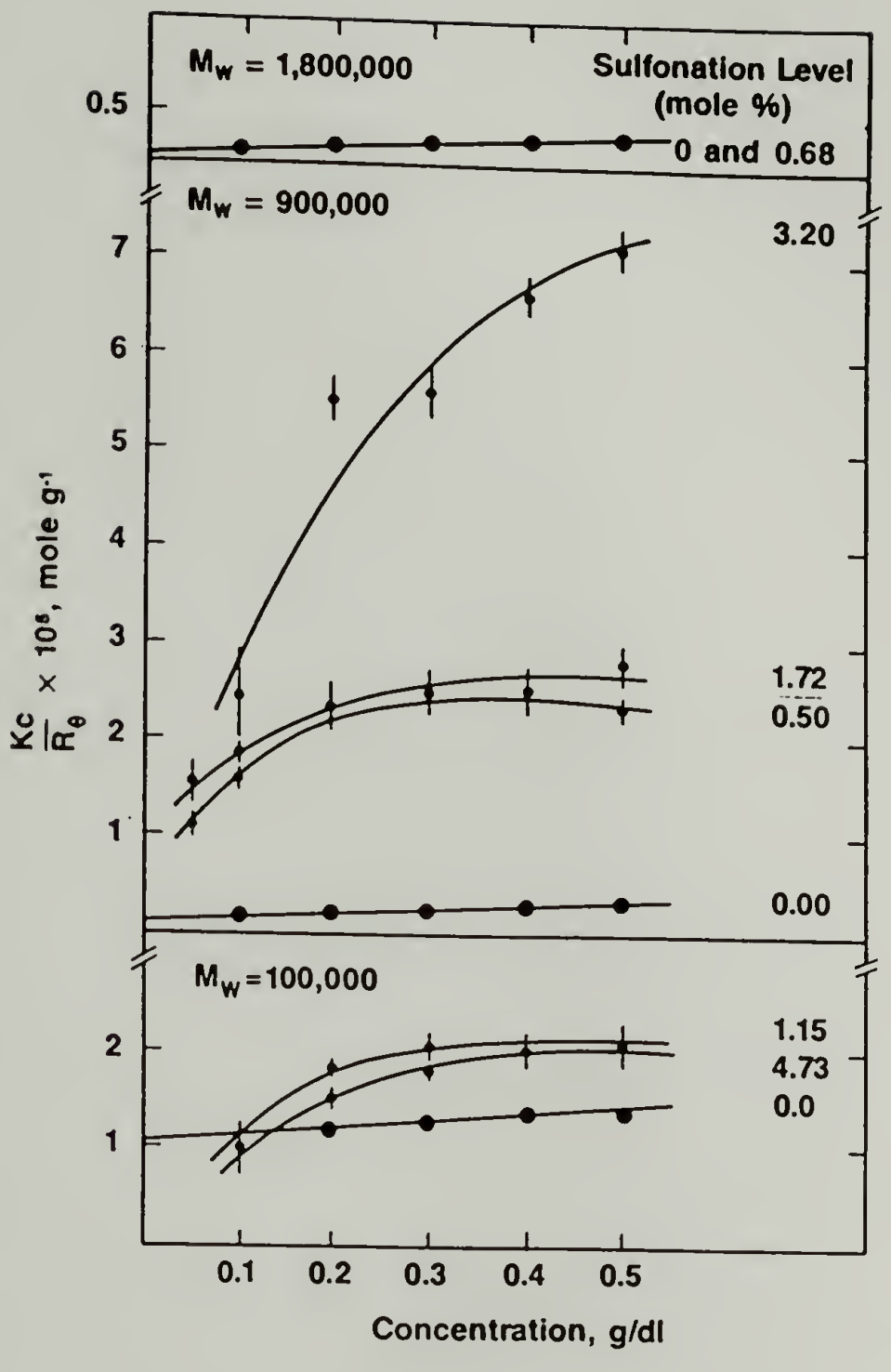

Figure 14. Static small-angle light scattering data for Na salts of sulfonated polystyrene dissolved in dimethyl formamide.

Table 8. Static Light Scattering Results for PS/DMF Solutions.

Molecular Weight (g/mol)	Measured Molecular Weight (g/mol)	$A_2 \times 10^6$ (dl mol g^{-2})
100,000	95,000 ± 9,500	3.8 ± .4
900,000	952,000 ± 95,000	1.9 ± .2
1,800,000	1,877,000 ±198,000	1.8 ± .2

Table 9. Quasi-elastic Light Scattering Results for SPS/DMF Solutions

Counterion	$D_T \times 10^7$ ($cm^2 s^{-1}$)
Na	2.8 ± .2
Zn	2.0 ± .2
H	2.3 ± .2

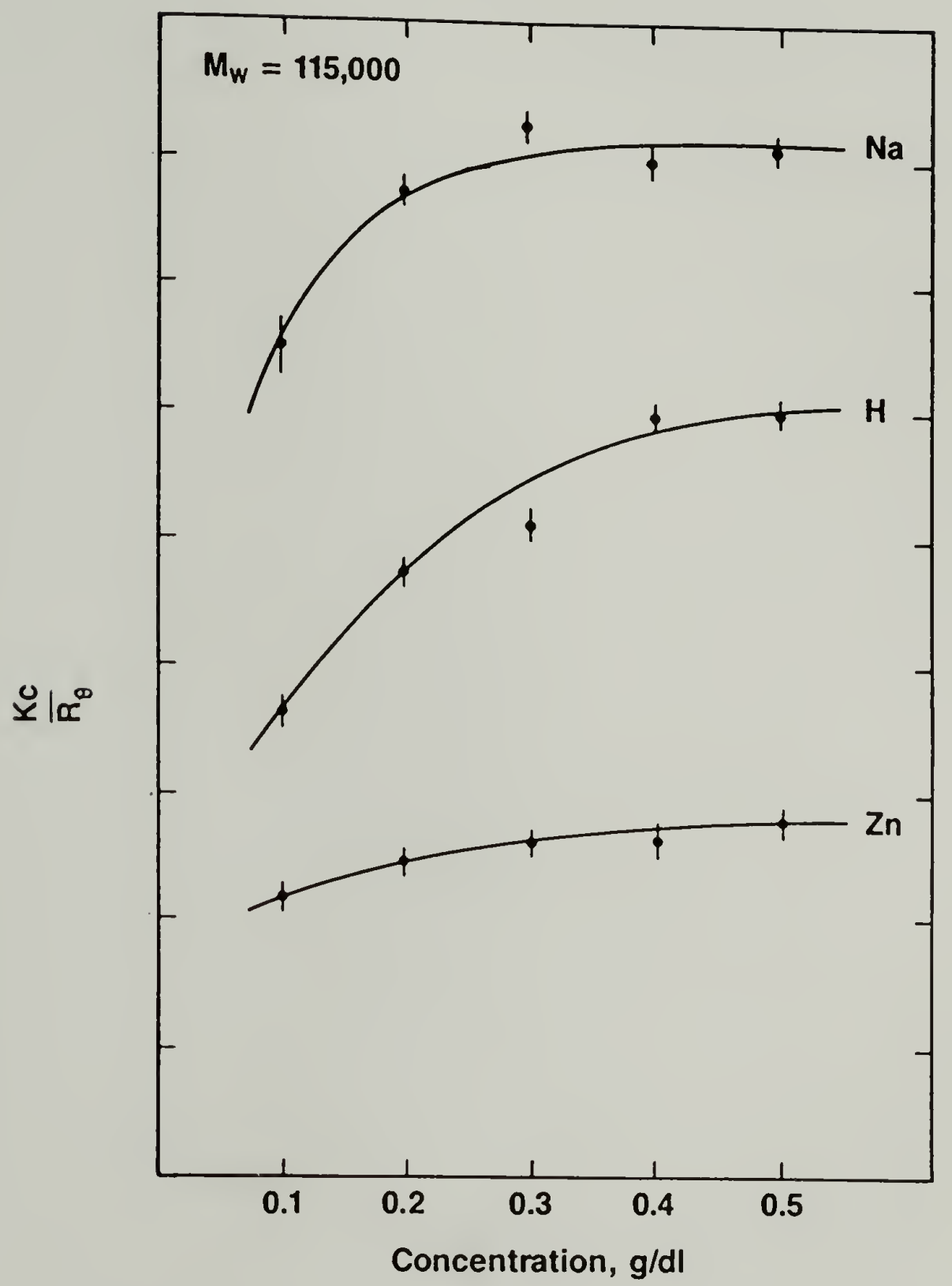

Figure 15. Static small-angle light scattering data for sulfonated polystyrene (2.49 mol%S) dissolved in dimethyl formamide.

again indicated by the low diffusion coefficients as measured by QELS. The amount of chain expansion increases in the order Na < H < Zn. These results are consistent with other measurements on sulfonate-based ionomers. The specific data are collected in Table 9.

The results from QELS and SALS support the presence of polyelectrolyte behavior in SPS ionomer solutions in DMF but do not provide a molecular basis for the phenomenon. In order to further investigate this behavior, the small-angle neutron scattering from analogous solutions in perdeuterated DMF was measured at a fixed concentration. The resulting scattering curves are shown in Figures 16 - 18. The presence of a peak in the small-angle scattering is consistent with the assignment of polyelectrolyte behavior to the viscosity.[38,39] This peak moves to smaller angles with increasing molecular weight and is not observed in the angular range measured for the highest molecular weight. Its presence at the highest sulfonation level suggests that interference effects are present which may not be negligible at lower ionic contents. Though several theories have been developed to explain the polyelectrolyte peak,[33-35,40-42] it is not possible to unambiguously derive single chain information from the data in Figures 16 - 18.

In order to obtain single chain information from these polyelectrolyte solutions, mixed labelling experiments were performed. Ionomers with a fixed molecular weight of 50,000 g mol^{-1} were studied

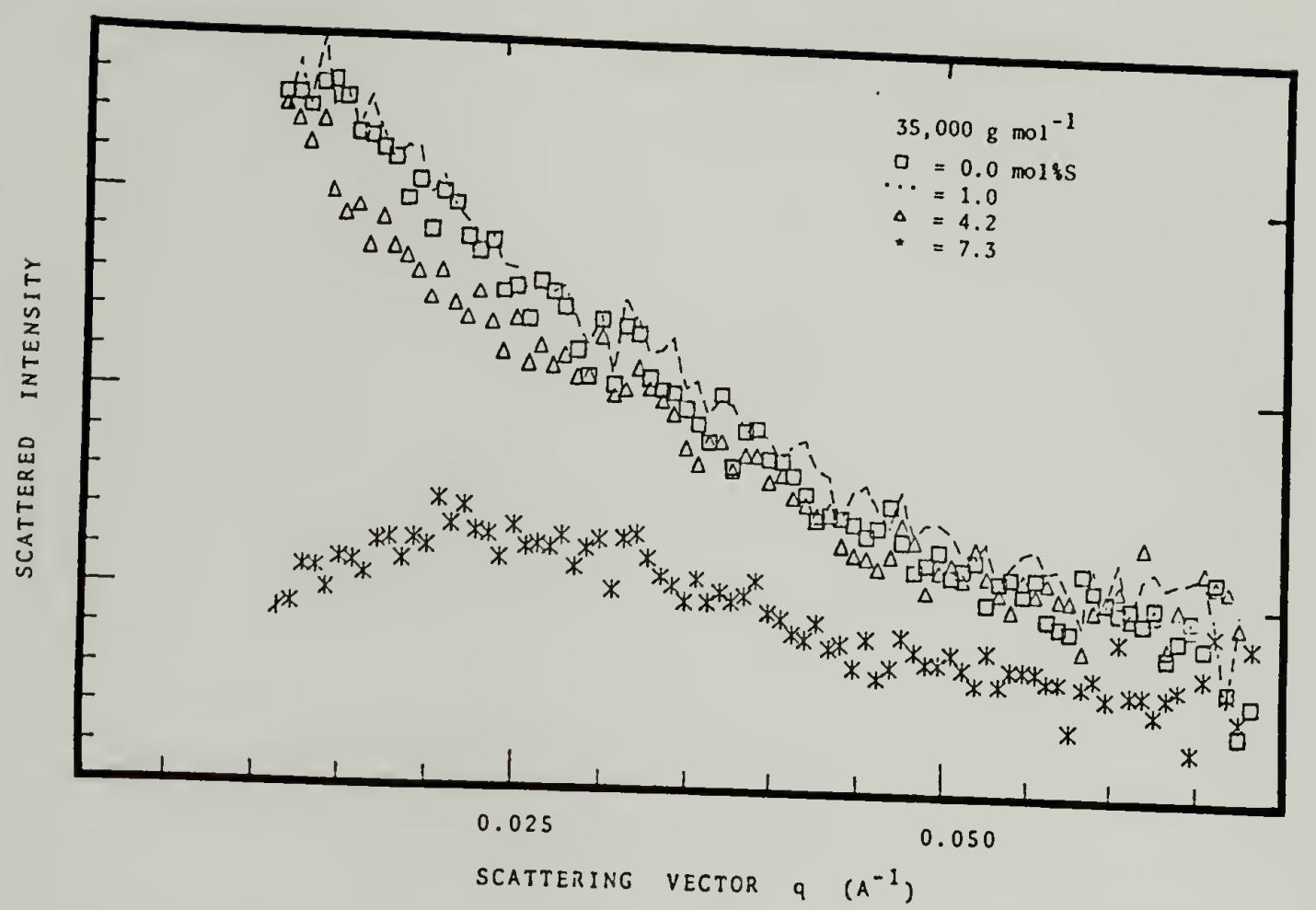

Figure 16. Small-angle neutron scattering data for Na salts of hydrogenous sulfonated polystyrene dissolved in perdeuterated dimethyl formamide (0.5 g dl; 35,000 g mol).

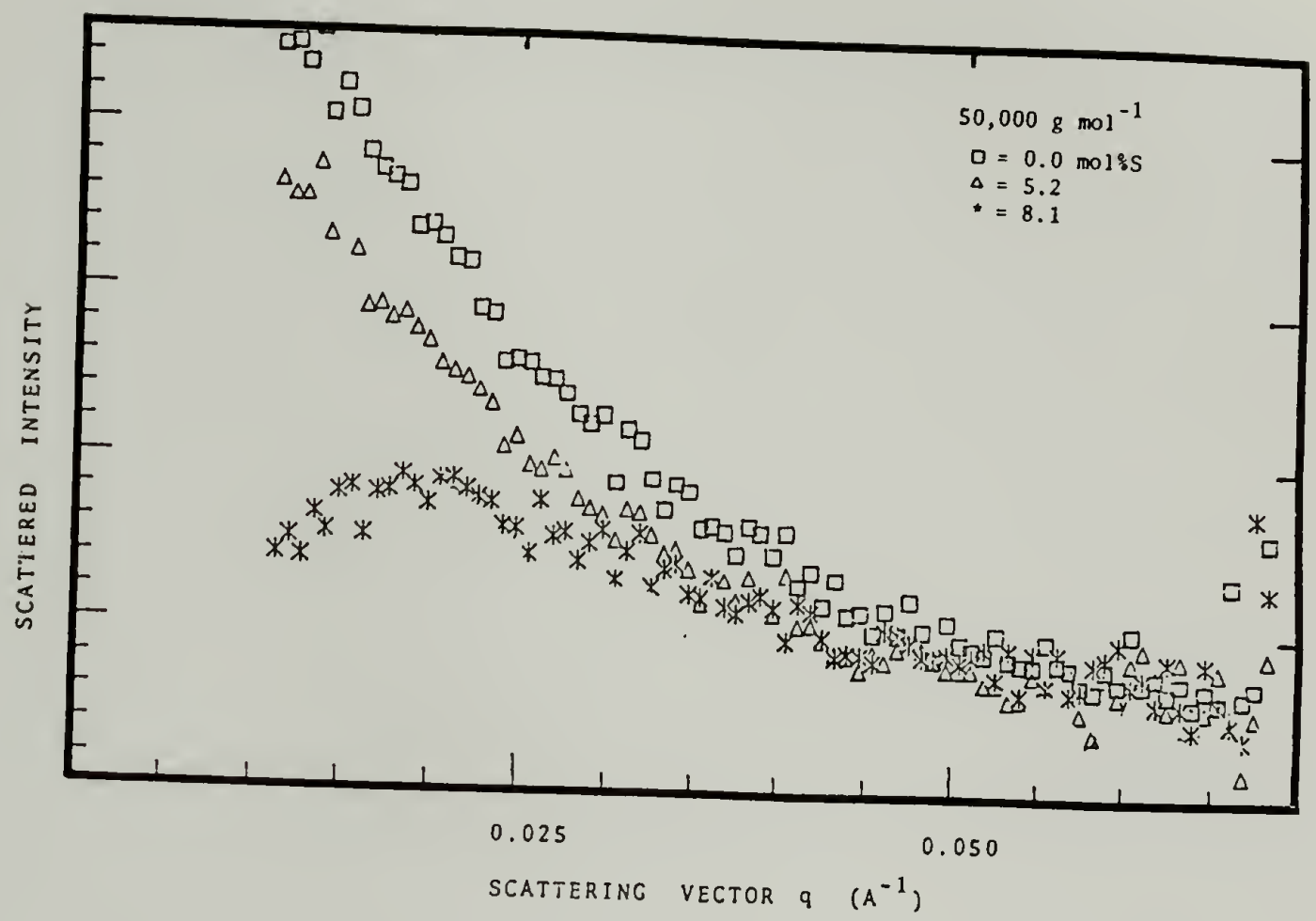

Figure 17. Small-angle neutron scattering data for Na salts of hydrogenous sulfonated polystyrene dissolved in perdeuterated dimethyl formamide (0.5 g dl; 50,000 g mol).

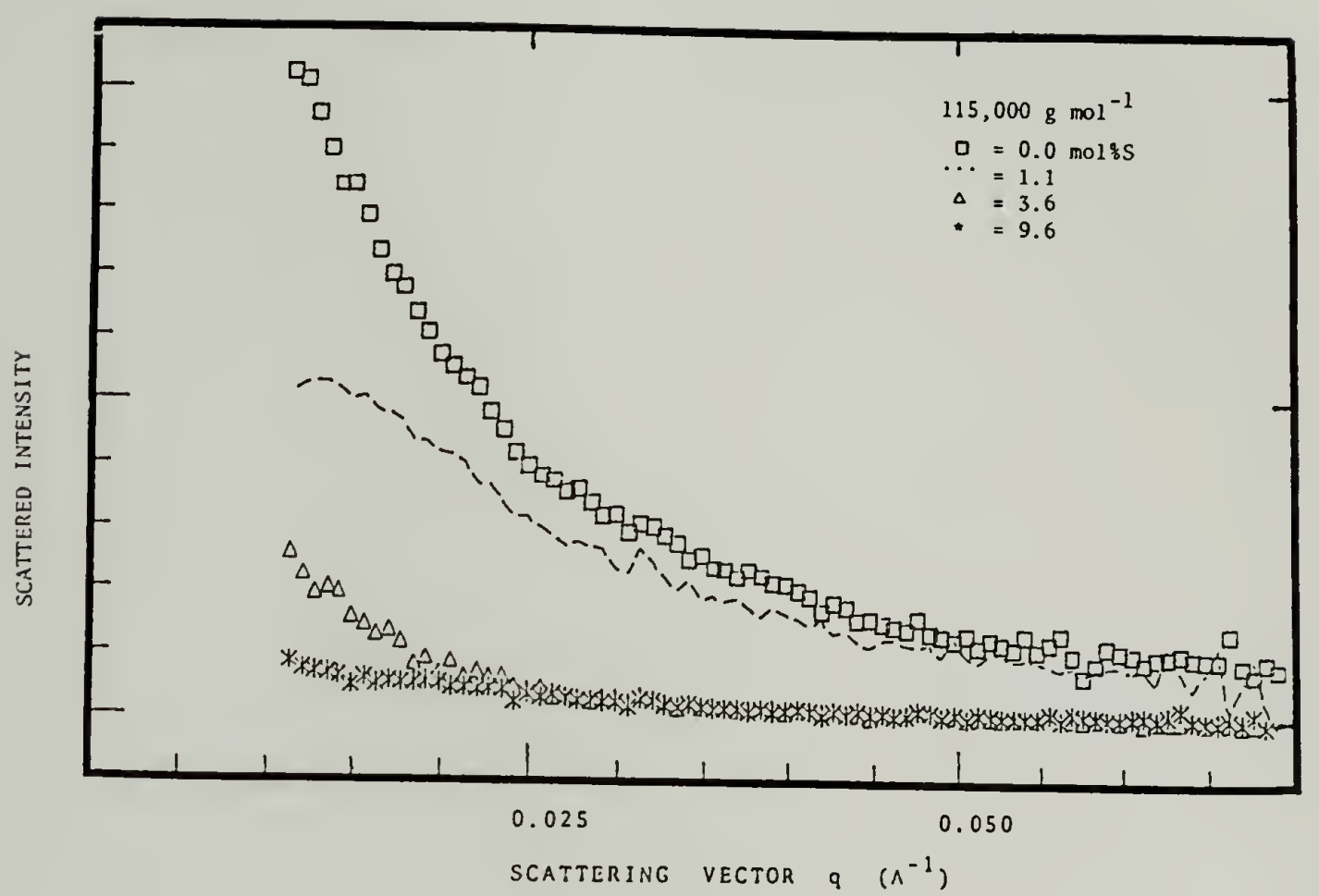

Figure 18. Small-angle neutron scattering data for Na salts of hydrogenous sulfonated polystyrene dissolved in perdeuterated dimethyl formamide (0.5 g dl; 115,000 g mol).

over a range of sulfonation levels and polymer concentrations. An example of the mixed labelling subtraction is shown in Figure 19 where the scattering from a solution of hydrogenous ionomers is compared with that of a solution containing both hydrogenous and perdeuterated chains. These two scattering curves are combined to yield the single chain form factor. The result shows clearly that the polyelectrolyte peak is due to interference between chains since it is absent from the single chain profile. This is in agreement with preliminary studies on aqueous solutions of classical polyelectrolytes.[43]

The resulting scattering curves for the ionomer solutions are shown in Figures 20 and 21 while the corresponding single chain scattering appears in Figure 22 and 23. The scattering from the unmodified polystyrene precursor was also measured for comparison. The scattering from PS of known molecular weight was used to scale the ionomer scattering curves in order to obtain absolute intensity data.

Molecular parameters were determined by use of equation 7. The resulting plots are shown in Figures 24 and 25 and the values of R_g and M obtained are listed in Table 10. Due to the nature of the subtraction technique, no correction for A_2C_p is required for the single chain data. This is not true of the total scattering from the unmodified PS dissolved in dDMF however. The value of $A_2=3.8\times10^{-4}$ $cm^3 mol\ g^{-2}$ was estimated for this solution from light scattering measurements. As a check, the data was also fit with equation 9 which does not require an

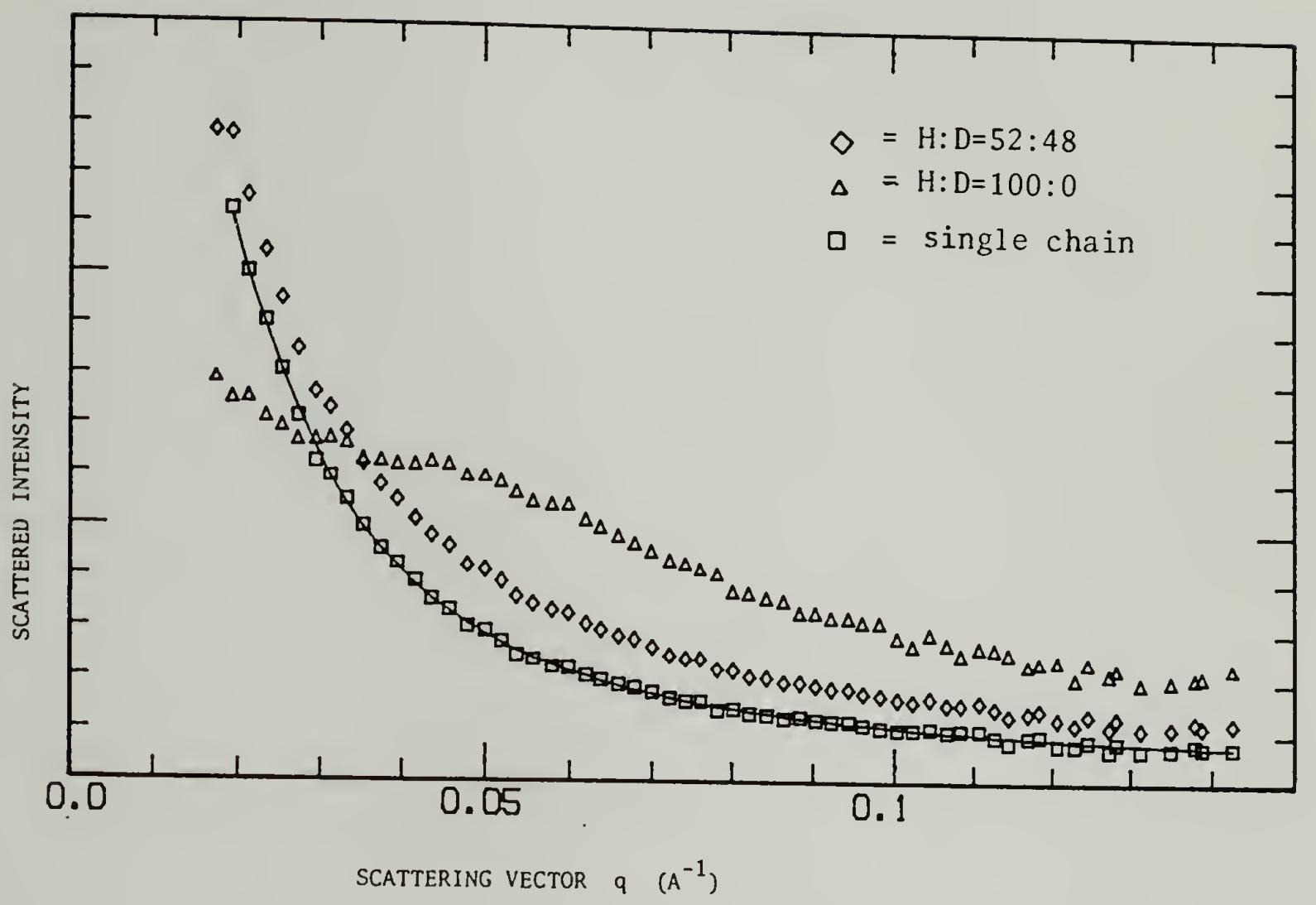

Figure 19. Mixed labelling subtraction technique in dimethyl formamide.

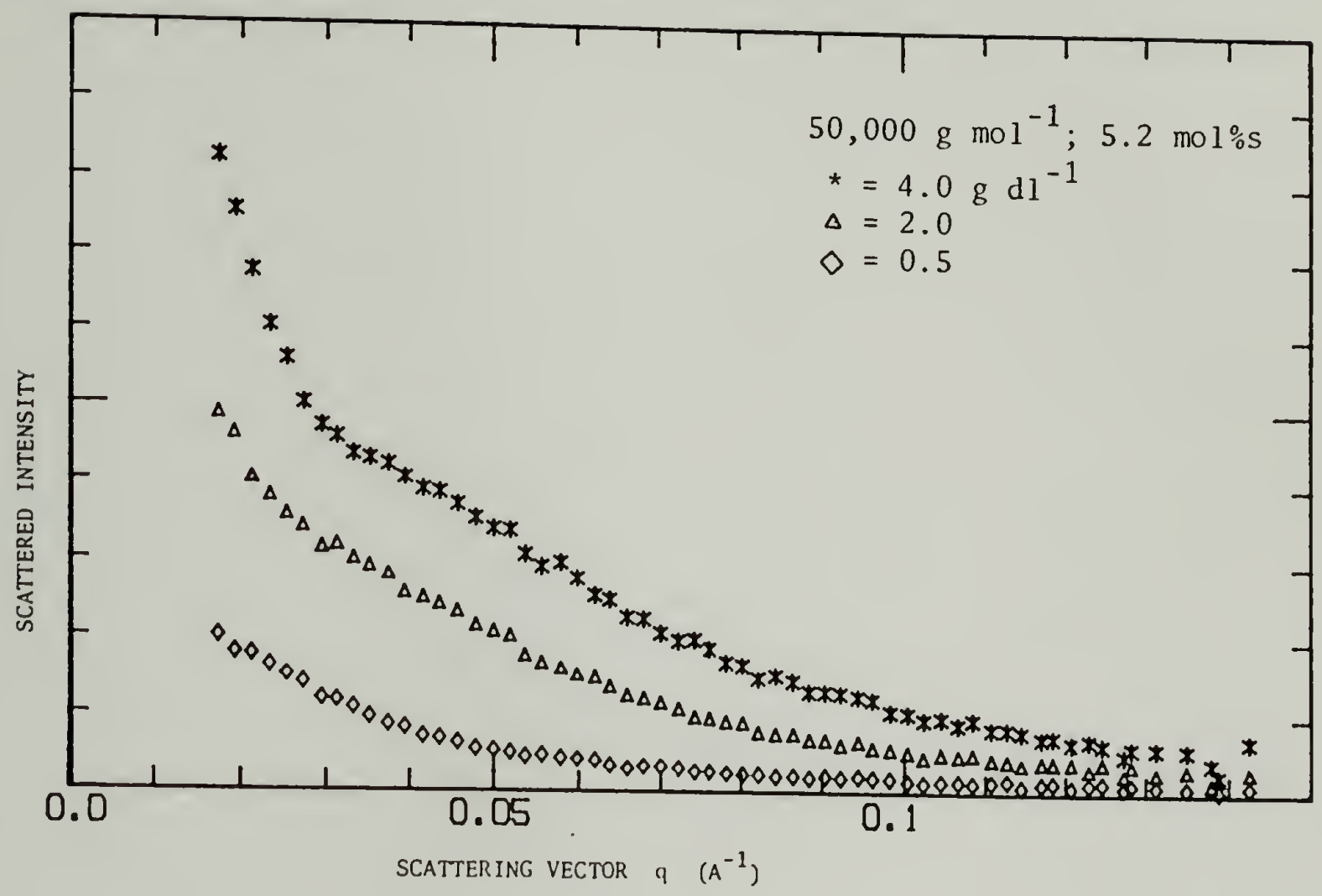

Figure 20. Small-angle neutron scattering data for Na salts of hydrogenous sulfonated polystyrene dissolved in perdeuterated dimethyl formamide.

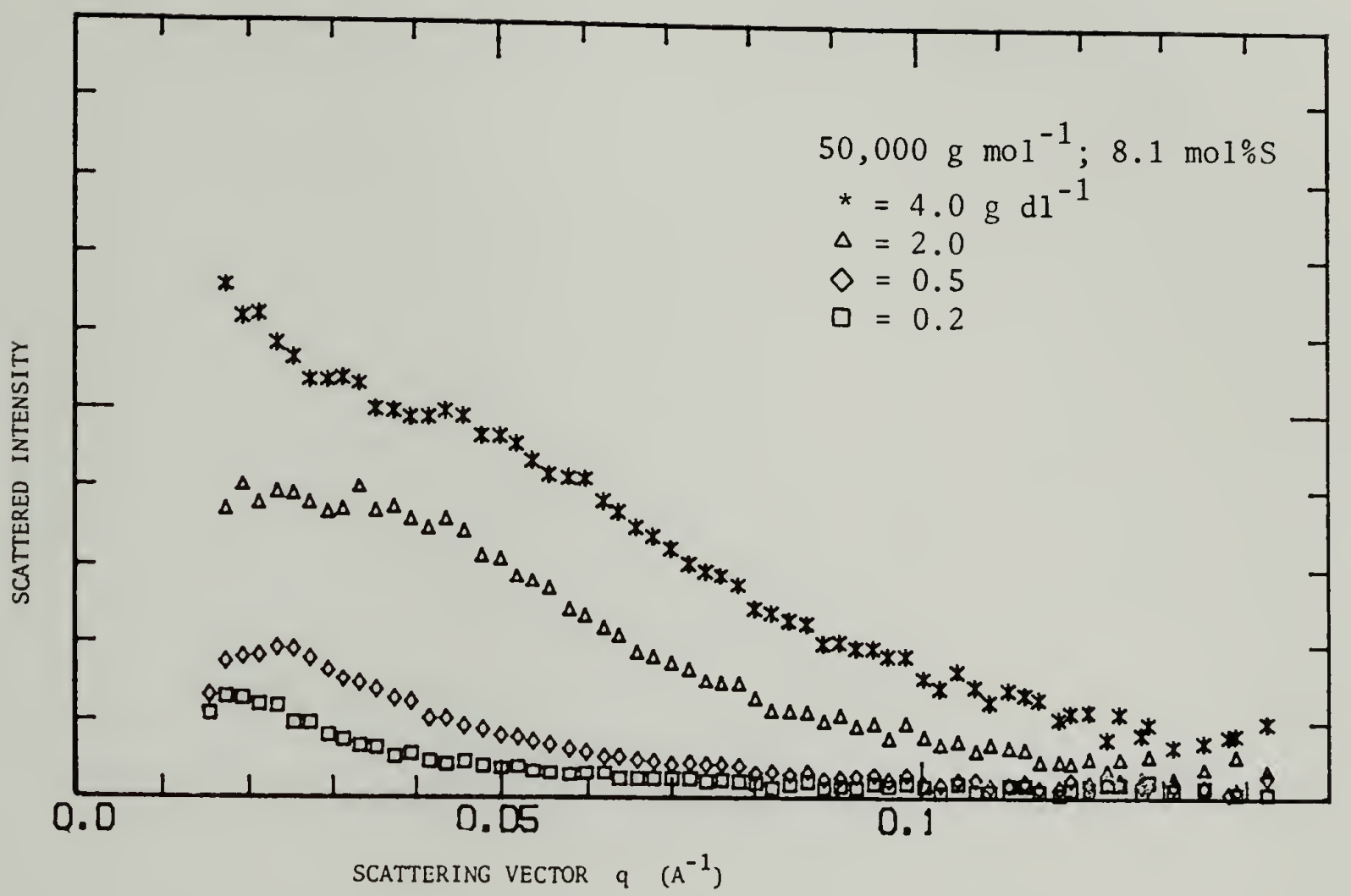

Figure 21. Small-angle neutron scattering data for Na salts of hydrogenous sulfonated polystyrene dissolved in perdeuterated dimethyl formamide.

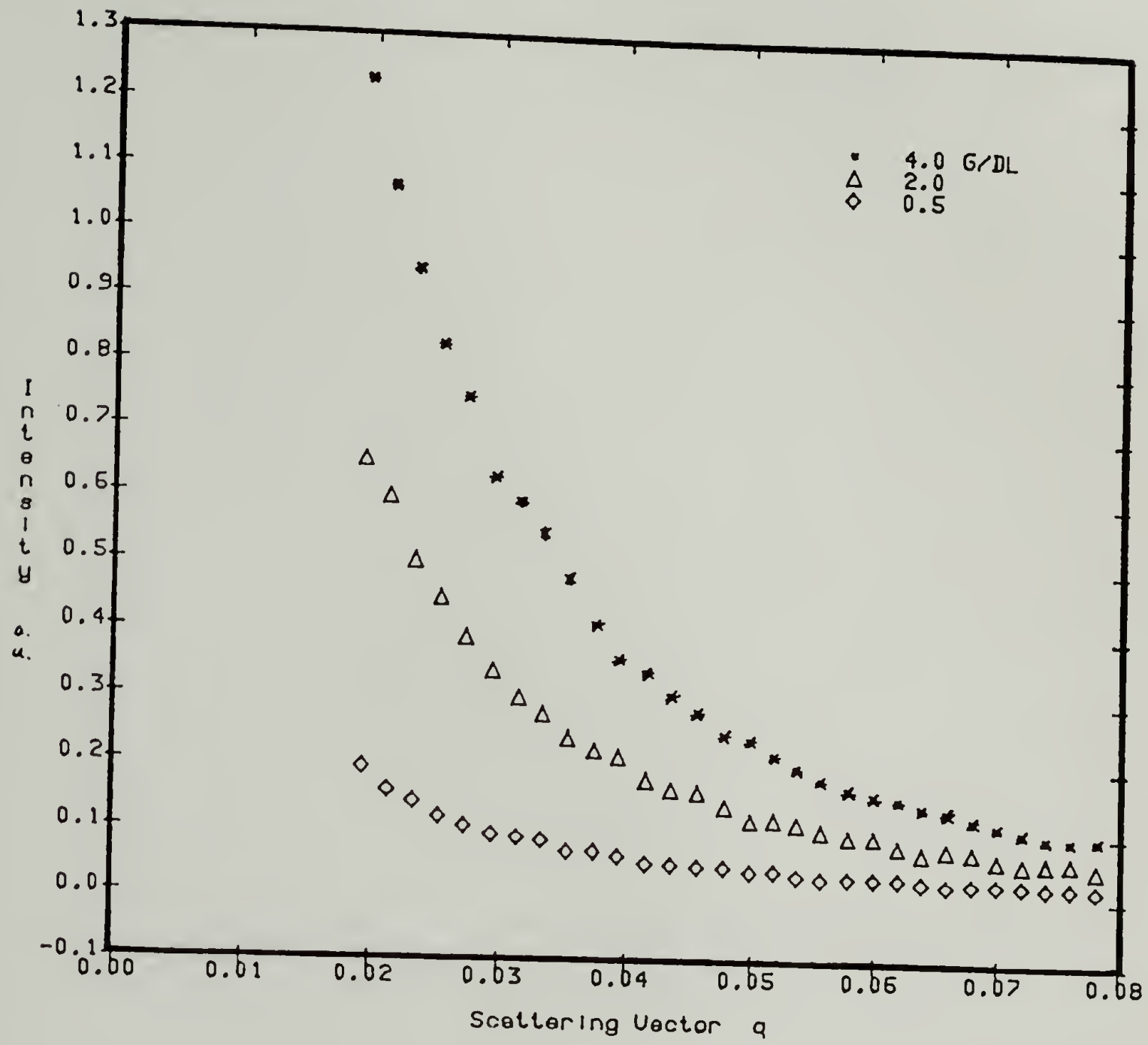

Figure 22. Calculated single chain scattering for the data in Figure 20.

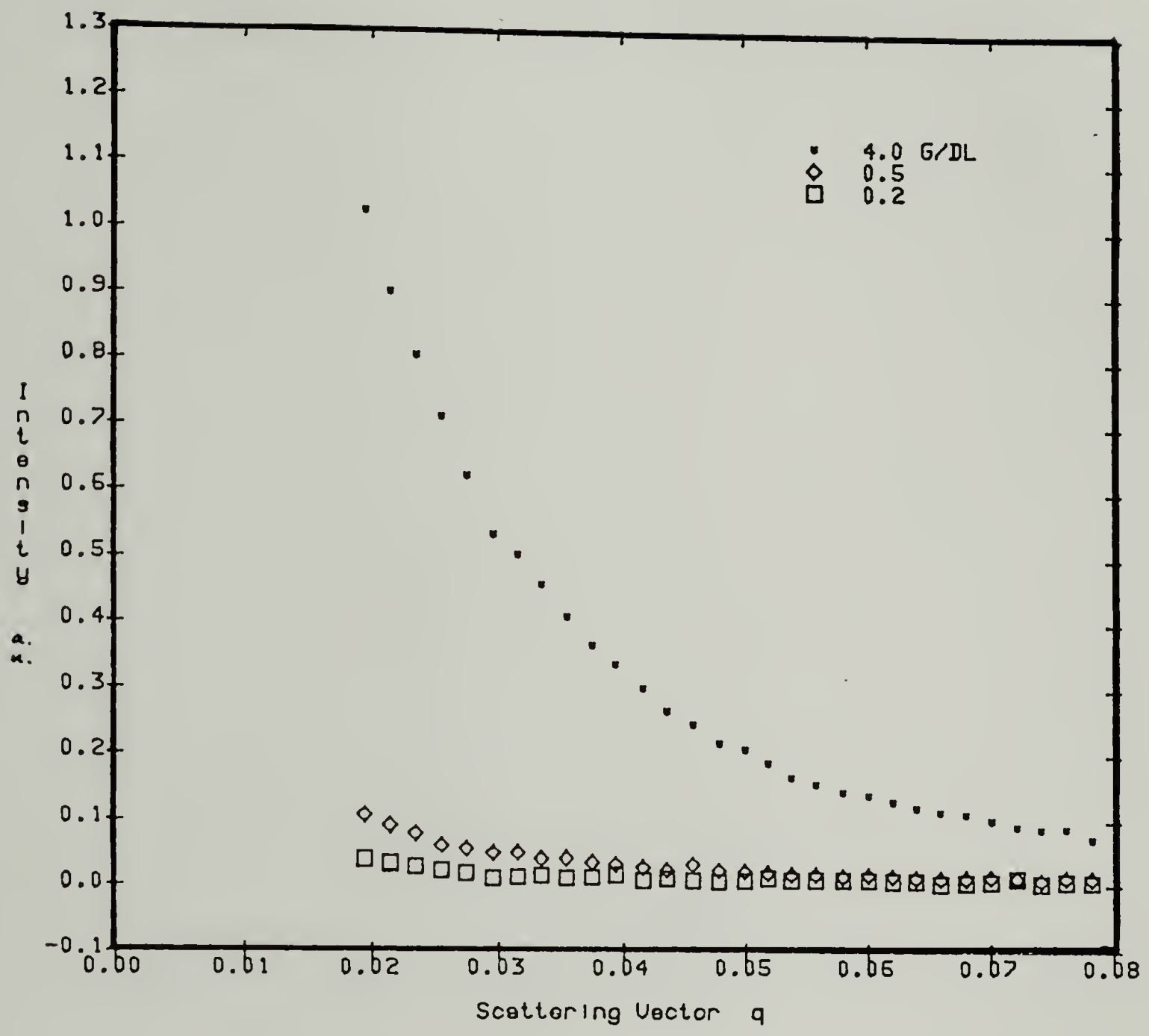

Figure 23. Calculated single chain scattering for the data in Figure 21.

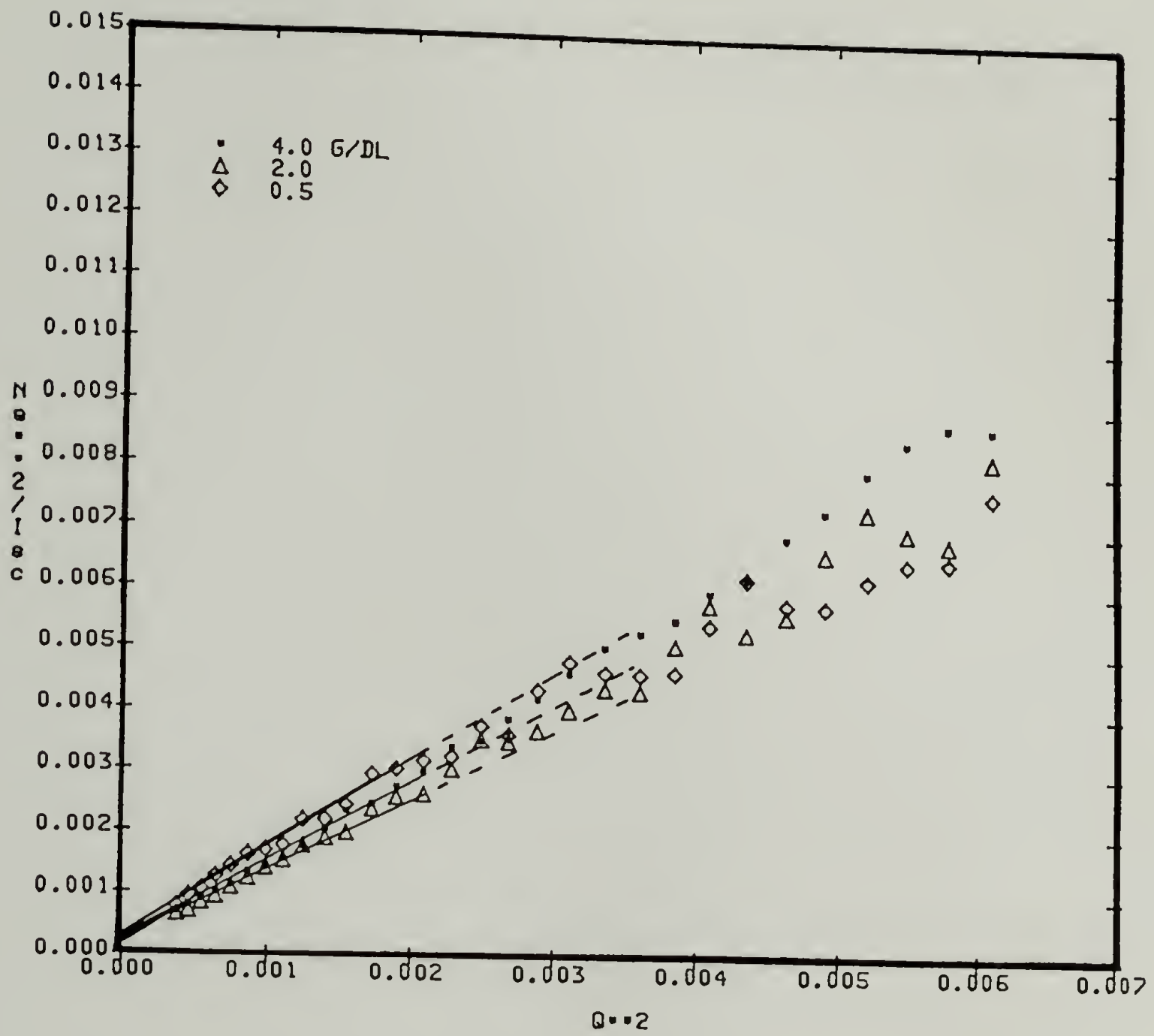

Figure 24. Zimm analysis of the calculated single chain scattering for the data in Figure 20.

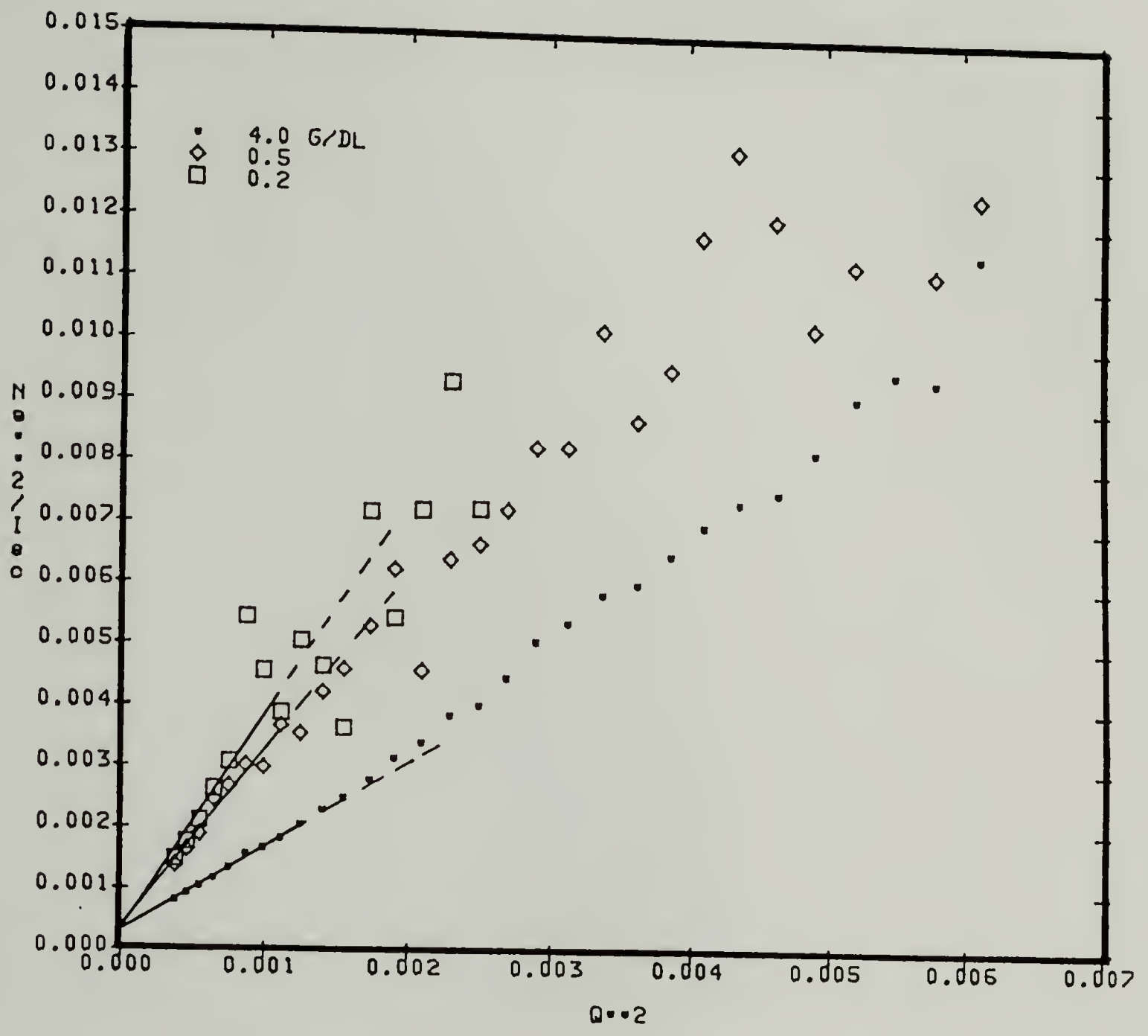

Figure 25. Zimm analysis of the calculated single chain scattering for the data in Figure 21.

Table 10. Single Chain Parameters for SPS/DMF Solutions. Zimm Analysis of SANS Data.

System	Concentration	Rg (A)	Mw (g/mol)	n
PS 50,000	0.5 g/dl	66 ± 6	assumed 50,000	2.0
SPS 50,000 5.2 mol%S	4.0	127 ± 13	40,000 ± 4,000	1.8
	2.0	119 ± 13	40,000 ± 4,000	1.8
	0.5	136 ± 14	40,000 ± 4,000	1.6
SPS 50,000 8.1 mol%S	4.0	128 ± 13	40,000 ± 8,000	1.8
	0.5	189 ± 19	40,000 ± 8,000	1.7
	0.2	209 ± 21	40,000 ± 8,000	1.4

Table 11. Infinite Dilution Dimensions of SPS/DMF.

System	L (A)	Rg (A)	C^* (g/dl)
SPS(5.2%)	840	240	0.014
SPS(8.1%)	1030	300	0.008

estimate of A_2. Estimates of the zero-angle intensity and scattering baseline were iteratively improved and the resulting fit is shown in Figure 26. It yields a value of 70A for R_g which is in excellent agreement with that calculated with the estimated A_2 value and listed in Table 10.

The molecular weight of a single ionomer chain should, of course, remain constant with variation in concentration. A value which is constant within experimental error is measured by the subtraction technique as can be seen in Table 10. The values of R_g in Table 10 indicate that chain expansion does indeed occur at sufficiently low polymer concentrations. This is consistent with the reduced viscosity measurements shown in Figure 11.

The actual chain conformation is naturally of great interest. To estimate this geometry, the doubly logarithmic plots shown in Figure 27 were constructed. It should be recalled that the scattering from a polymer chain can be described as

$$I(q) \sim q^{-n} \qquad (16)$$

where the exponent n has a value of 2 for a random coil and a value of 1 for a rigid rod.[29] The measured values of n are given in Table 10. As can be seen, polystyrene exhibits the expected coil-like behavior. The

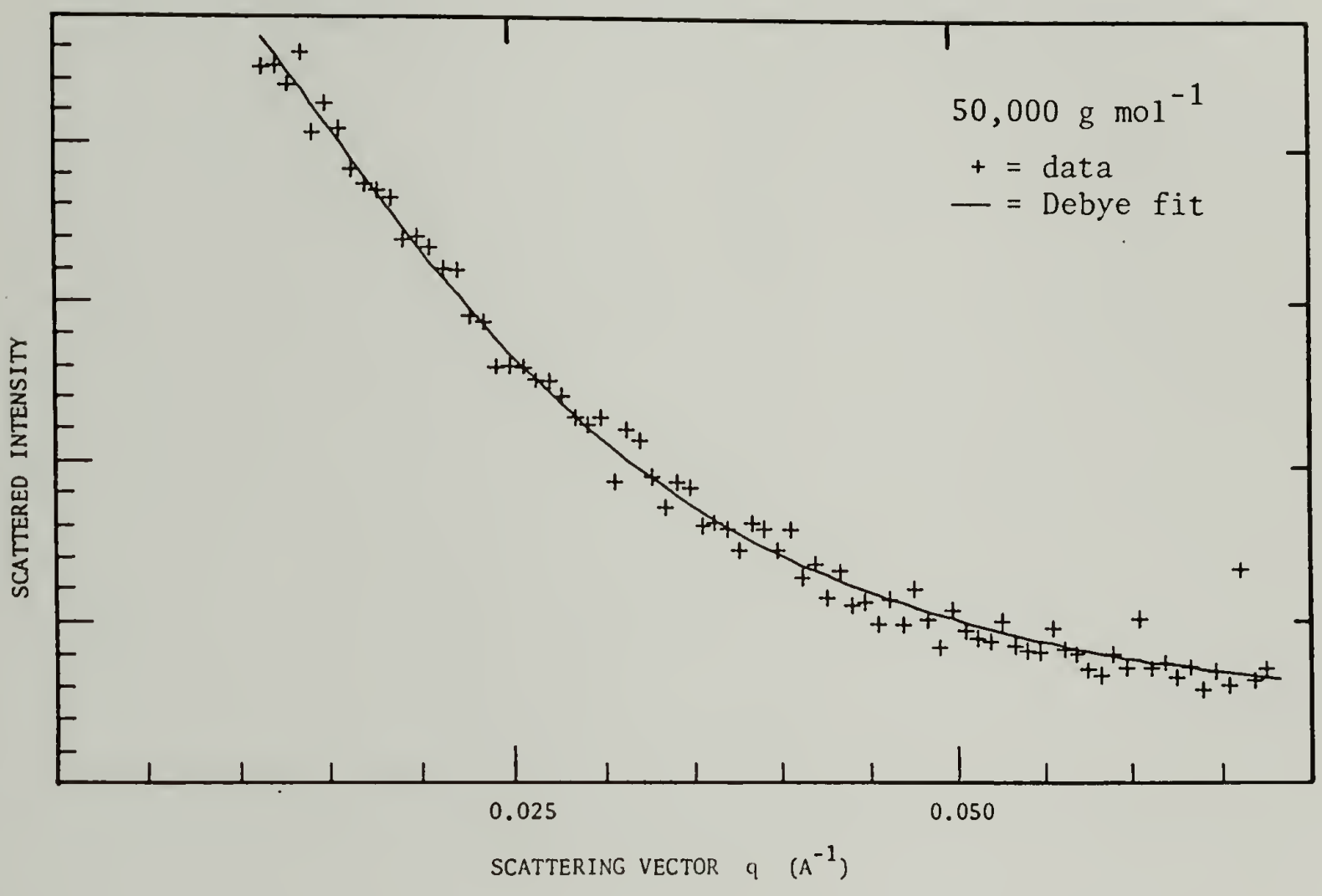

Figure 26. Small-angle neutron scattering data for hydrogenous polystyrene dissolved in perdeuterated dimethyl formamide (0.5 g/dl) and Debye theoretical fit.

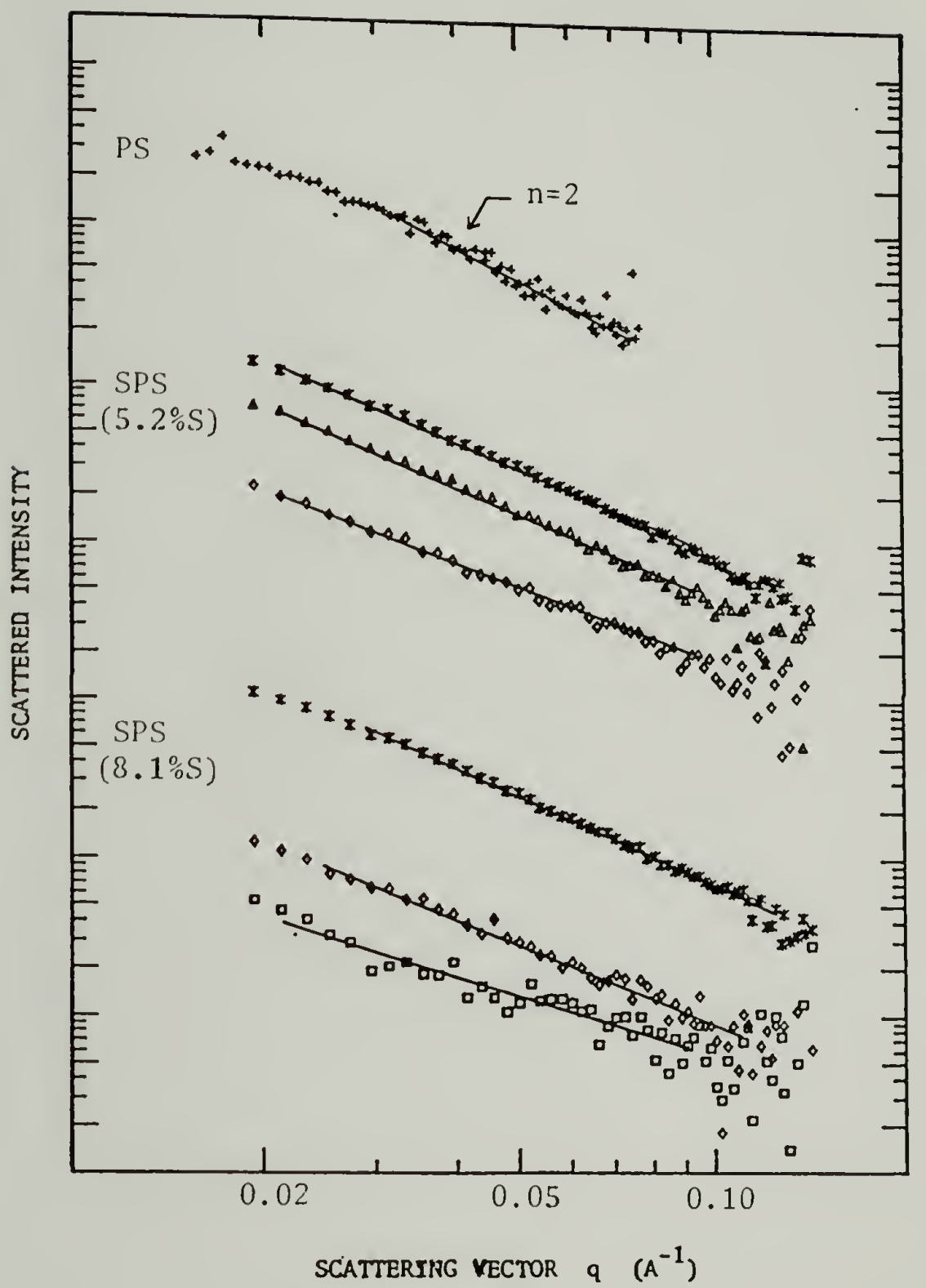

Figure 27. Double logarithm plots of the data of Figures 26, 23 and 22. Plots displaced vertically for clarity. Symbols used as defined previously.

ionomer chains, however, are intermediate between rods and coils and become more rodlike with decreasing polymer concentration.

These results can be used to model the ionomer chains in the following way. First the measured R_g of the PS chain is used to determine a statistical step length l for a PS random coil. Using the well-known relation,[31]

$$\langle R_g^2 \rangle = \frac{nl^2}{6} \tag{17}$$

where the number of steps n is set equal to the ratio of polymer to monomer molecular weight, yields a value of l=7.5Å. It is then assumed that each charge along an ionomer chain is separated by a random walk of m steps where m is the reciprocal of the average percent ionic content. Hence the ionomer will be locally "wiggly" at length scales less than $(ml^2)^{1/2}$ but stiff at larger length scales. In dilute polar conditions, electrostatic repulsions between charges would force the polymer chain to form a rod of length L where

$$L = \frac{n}{m}(ml^2)^{1/2} \tag{18}$$

This is depicted schematically in Figure 28. Knowing the molecular weight, sulfonation level and statistical step length, it is possible to calculate values for the infinite dilution rod length L. Once L is known, the overlap concentration C^* can be estimated as $C^* = M/(L)^3$. The

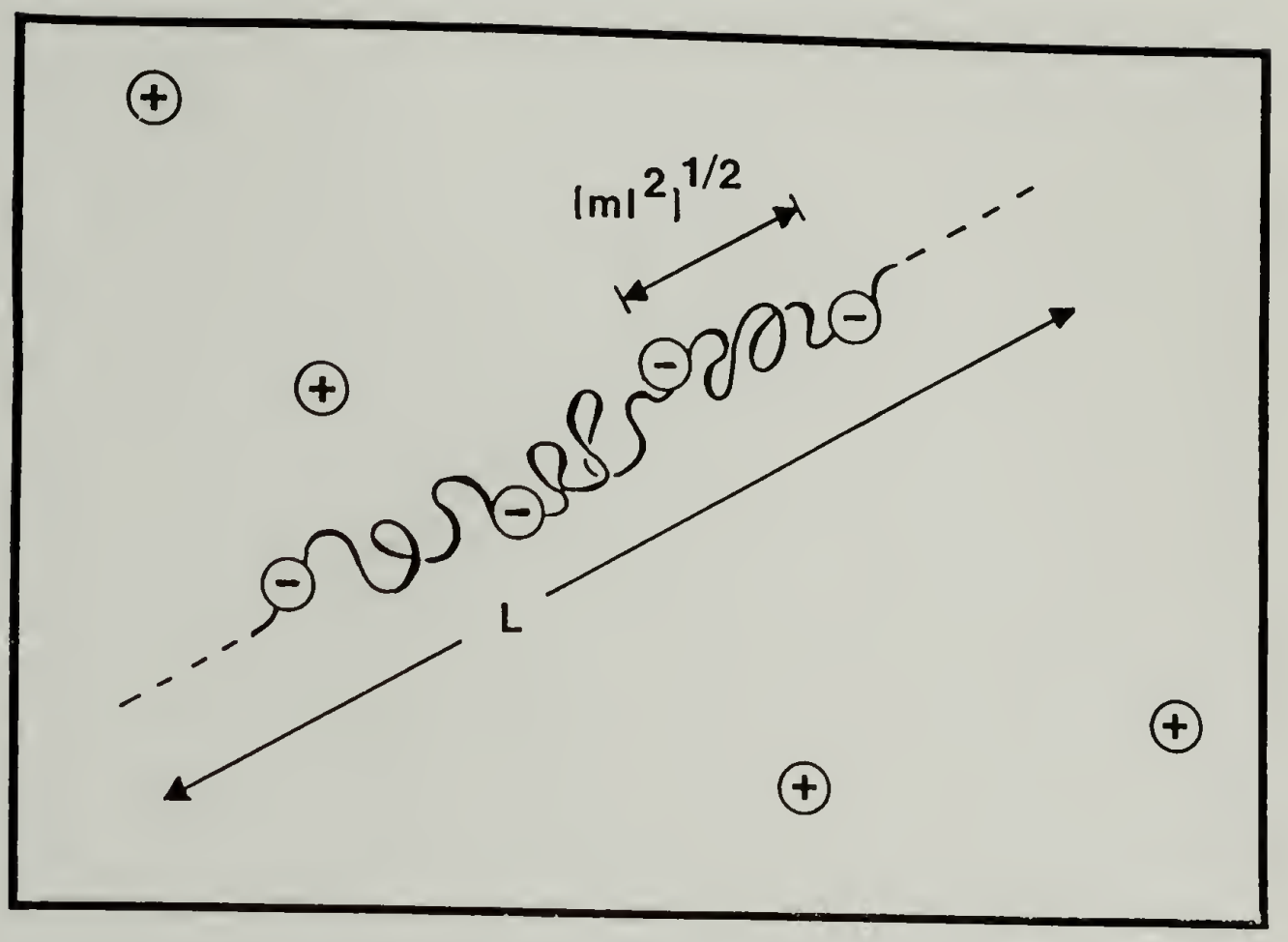

Figure 28. Schematic of an ionomer at infinite dilution in an ionizing solvent.

radius of gyration for this infinite dilution limit can also be calculated as $R_g^2=L^2/12$. The results of these calculations are given in Table 11. With the assumptions of this model, the results show that even the lowest concentration studied is above the overlap concentration.

Since these ionomer solutions are sufficiently concentrated for one chain to be affected by the presence of another, it is expected that screening will cause the ionomer chain to deviate from purely rodlike behavior.[44] Hence the measured radius of gyration is expected to be less than the infinite dilution dimensions calculated above. At the highest concentration of this study (4.0 g dl^{-1}), this screening leads to comparable chain dimensions for both the 5.2 and 8.1 mol%S ionomers. As polymer concentration decreases, the screening effect of the surrounding chains diminishes and hence the ionomer may traverse longer rod-like paths. The resulting increase in R_g is particularly evident at the higher sulfonation level in Table 10. Even at the lowest concentration studied however, the measured R_g does not attain the full theoretical value of an individual unscreened rod. The resulting picture of ionomers in polar solvents is one of partially straightened chains which are forced to deviate from purely rodlike behavior by the screening of interactions by neighboring chains. This interpretation is consistent with the results in Figures 27 and with recent theoretical work.[42]

CONCLUSIONS AND FUTURE STUDIES

Using a model ionomer system, ionomer soluton properties have been studied by static and quasi-elastic light scattering, small-angle neutron scattering and solution viscosity measurements. Specifically, lightly sulfonated polystyrene ionomers of narrow molecular weight distribution have been studied in two very different solvent environments. The effects of solvent polarity, as well as molecular weight, counterion and polymer concentration have been determined. The results show that ionomer solution behavior naturally divides into two types: polyelectrolyte and associating polymer.

Ionomers dissolved in an ionizing solvent such as dimethyl formamide exhibit a pronounced polyelectrolyte effect. This is manifested by non-linear relationships in reduced viscosity - concentration profiles and in the static light scattering data. Thus, even in this non-aqueous solvent, a sufficient degree of ionization occurs to cause chain expansion via the mutual repulsion of negatively charge sulfonate groups. The quasi-elastic light scattering measurements corroborate this interpretation.

Small-angle neutron scattering studies of lightly sulfonated polystyrene ionomers dissolved in perdeuterated dimethyl formamide

verify the presence of polyelectrolyte behavior at low polymer concentrations. Within these non-dilute solutions, single chain information has been extracted by a mixed labelling technique. The results reveal partial chain expansion upon dilution, in agreement with theoretical predictions. Presumably, a sufficient number of the sodium salt groups are dissociated in this highly polar solvent to cause chain expansion. This chain expansion is shown to be mitigated by the presence of other ionomer coils; hence the purely rodlike limit is never observed.

Distinctly different behavior is observed in non-ionizing solvents. In comparison to the marked ionomer chain expansion observed in dimethyl formamide, ionomer coil association is observed at low polymer concentrations in tetrahydrofuran. As concentration increases, intermolecular associations result in aggregation and eventually gelation. This aggregation phenomenon in non-ionizing solvents is clearly observable by quasi-elastic light scattering. It is also manifested by the decrease in the second virial coefficient as measured by static light scattering.

Small-angle neutron scattering studies of sodium salts of lightly sulfonated polystyrene in perdeuterated tetrahydrofuran verify the presence of associating polymer behavior in ionomer solutions with non-ionizing solvents. The scattering results provide a molecular basis for the solution viscosity behavior. Individual ionomer coils are observed

to retain constant dimensions while associating to form multi-coil aggregates. At this low level of sulfonation, the single coil dimensions within an aggregate are not significantly different from those of unmodified polystyrene. Inter-chain associations are found to persist to unexpectedly low concentrations. The extent of aggregation is observed to be very dependent on concentration in agreement with light scattering and solution viscosity studies.

Finally, it should be noted that these results from narrow molecular weight distribution sulfonated polystyrene ionomers clarify, to a great extent, the previously reported solution viscosity measurements on polydisperse materials. It is anticipated that these findings will be useful in interpreting the solution properties of ion-containing polymers in general and sulfonate-based ionomers in particular.

As is so often the case, this investigation has spawned several new questions. To address these questions, the following studies are recommended. The most obvious extension of this study is to broaden the concentration range of measurement. Truly dilute conditions where pure single chain behavior is observed were not reached in the current study and are of great interest. In non-ionizing solvents, this condition should present the limiting case of purely intra-molecular associations. In the case of ionizing solvents, the dilute limit should mimic

polyelectrolytes in the absence of screening effects - a physical state rarely obtained in classical systems. Such measurements would be of great value in extending existing theories for ion-containing polymer solutions. The experimental feasibility of obtaining the truly dilute state is uncertain. This study indicates that concentrations of 0.05 g dl^{-1} and lower must be measured; hence the method of choice would be light scattering due to the high intensity of the laser source. The drawbacks of this technique are the inability to do mixed labelling experiments and the need for ultra-clean solutions to avoid scattering from extraneous dust particles.

Conversely, measurements of concentrated solutions would also be of interest. The current measurements were performed on solutions at the threshold of polymer overlap. It would be valuable to perform studies at higher concentrations in order to understand the change-over from solution to solid state morphology and the accompanying change in properties. In non-ionizing solvents, this solidification process may occur as an extension of the gelation phenomenon seen in the current study. In the case of ionizing solvents where the chains are mutually repelled however, the mechanism of solidification is more difficult to envision. Measurements of concentrated solutions are clearly needed. The preferred method for studying these solutions is small-angle neutron scattering since it alone allows the measurement of single chain dimensions within concentrated systems.

With the increased understanding of ionomer solutions which hopefully is gained by this discussion and the proposed future studies, it will be important to study the interactions between ionomer solutions and solid surfaces. Due to the inclusion of ionic groups, these materials are expected to be sensitive to surface polarity and therefore to surface energy. As a result, it may be possible to tailor ionomer composition to produce a desired surface effect. Again, small-angle neutron scattering studies should be done to determine chain conformation at the solution/solid interface. Fundamental physical chemical measurements such as infra-red spectroscopy, photoelectron spectroscopy and contact angle goniometry will important. The results should address basic questions of polymer-surface interactions.

Discussion thus far has focused on the behavior of the polymer backbone in ionomer solutions. The behavior and location of the ionic species are clearly of importance as well. Small-angle x-ray scattering studies of ionomer solutions should be undertaken for this reason. In the dilute concentration limit, such experiments may only be possible using synchrotron intensities and electron-dense counterions such as cesium. Preliminary studies indicate that ionomer solutions in the concentration range of the present study can be measured using a rotating anode x-ray source. Such measurements should be performed over the complete concentration range, bearing in mind the importance of sample history. These results would extend the current understanding of ionic structure in both solutions and solids.

A final and apparent comment is the need for the measurement of ionomer solution properties over a wider range of molecular weights and counterions. The exact effects of counterion identity are not yet known. Similarly, a larger range of molecular weights and ionic contents must be measured to evaluate the scaling theories which are currently being developed for both associating and polyelectolyte solutions.

CHAPTER II. SOLID STATE STUDIES

INTRODUCTION

During the three decades since synthetic ion-containing polymers were introduced,[45,46] these materials have remained of fundamental scientific interest as well as commercial use.[1-8] In these materials, the ionic nature of metallic salts and the covalent nature of hydrocarbon polymers are combined. This research focuses on polymer systems containing low amounts of ionic species. Such systems are generally dubbed "ionomers", a term brought into use by the DuPont company. Ionomer refers to a polymer composed of a hydrocarbon backbone containing pendant acid groups which are neutralized either partially or totally to the salt form. The fraction of salt groups is always less than that of the hydrocarbon backbone. In general, the term ionomer refers to such materials having less than ten mole percent salt groups. This clearly excludes classical polyelectrolyte materials as these contain salt species on every alternate backbone group. It is asssumed that the polar salt groups attempt to separate from the nonpolar hydrocarbon chains and that this separation is restricted by the chemical attachment of the salt to the chain. The resulting aggregates effectively crosslink the polymer and form a thermally labile network. Despite recent advances, the extent of microphase separation and hence the exact solid state morphology of ionomers remains an elusive problem.

One of the most striking characteristics of ionomers is their unconventional viscoelastic behavior. This was observed in the early work of Cooper.[47] When carboxylated rubbers were neutralized, the resulting salts exhibited some of the properties of vulcanized elastomers. This behaivior was first explained in terms of ionic crosslinking whereby a metal cation bridges two carboxylate groups and effectively links the associated chains. Subsequent studies suggest that a range of ionic associations is present. Several studies of viscoelastic ionomer properties have been undertaken in an effort to determine the nature of ionic crosslinking. There is a surprising amount of agreement between the results from different systems which suggests a universality of ionomer behavior.

The first attempt to predict the spatial arrangement of the salt groups in ionomers is the theoretical work of Eisenberg.[48] The fundamental structural unit is assumed to be the contact ion pair where the anion and cation are separated from each other by only their ionic radii. This assumption is shown to be a reasonable one since the work required to separate the ion pair in media of low dielectric constant is nearly two orders of magnitude greater than the available disruptive thermal energy. Associated ion pairs, triplets, quartets, et cetera in which the charges are as close to one another as possible are defined as **multiplets**. Three factors which govern the formation of multiplets are considered: 1) the dimensions of polymer chains and of ion pairs, 2) the tension on the chains resulting from ionic aggregation, and 3) the

electrostatic energy released upon multiplet formation. The possibility of multiplets to form **clusters** in which the multiplets are separated by non-ionic material is also considered. Thus a single ion pair can be regarded as the smallest possible multiple while the maximum multiplet size is governed by its geometry and the restriction that each ion pair must be attached to a hydrocarbon backbone. Clusters may be formed by the association of multiplets. This association is favored by electrostatic interactions between multiplets and opposed by the retractive elastic forces of the backbone chains.

The calculation of the maximum possible size for the multiplets is performed with the assumption of a spherical geometry where the attached hydrocarbon chains are restricted to the multiplet's surface. It then follows that the multiplet radius r_m is given by

$$r_m = 3v_p/s \tag{19}$$

where v_p is the volume of an ion pair and s is the area of the hydrocarbon chain in contact with the surface. For an ethylene-sodium methacrylate polymer, this leads to $r_m = 3A$ which suggests eight ion pairs per multiplet. Hence it is concluded that the multiplets cannot be very large if they are spherical, though such a conclusion does not hold for other geometries. In particular, if the multiplets are lamellar, there is essentially no limit to their size due to steric restrictions alone.

The formation of clusters will be driven by electrostatic interactions between multiplets. The nature of such interactions is governed by cluster structure. It is envisioned that cluster formation proceeds as follows. A multiplet of maximum size, approximately eight ion pairs, is completely covered by a hydrocarbon coating. Therefore it is impossible for another multiplet to approach by a distance less than the thickness of the coating, even though the multiplet of maximum size are expected to attract other multiplets through electrostatic interactions. Thus the cluster consists of a central core composed of a multiplet of maximum size surrounded at a distance by other multiplets of various sizes from ion pairs on up. The size of the cluster is limited by the elastic forces arising from the backbone chain which tend to "pull" the cluster apart.

The calculation of the electrostatic interactions is based on the assumption that energy is released when multiplets aggregate to form a cluster, the work depending on the dielectric constant of the medium and the geometry of the cluster. The opposing elastic forces are calculated on the basis of rubber elasticity theory. Since the elastic forces are proportional to temperature and the electrostatic forces vary only slightly with temperature, it is apparent that these two forces must balance at some critical temperature T_c above which clusters become unstable. Furthermore, it is suggested that a critical multiplet concentration for the formation of clusters exists since the elastic

forces will be greater than the electrostatic forces for small ionic concentrations.

The results of Eisenberg's calculations of the number n of ion pairs per cluster are

$$n = \rho \frac{N}{M} \left[\frac{4l^2}{3kT_c} \left[\frac{h^2}{h_o^2} \right]^2 \frac{M}{M_o} \frac{k'}{\kappa} \frac{e^2}{4\pi\varepsilon_o d} + 2 \left[\frac{M_o M}{\rho N} \right]^{2/3} \right]^{3/2} \qquad (20)$$

where ρ is the density; N is Avagadro's number; M is the molecular weight of the chain between pendant acid groups; M_o is the molecular weight per chain repeat unit; l is the length of a backbone bond; h^2 is the mean-square end-to-end distance for the free chain; h_o^2 is the mean-square end-to-end distance for a freely jointed chain; κ is the dielectric constant; $(1/4\pi\varepsilon_o)^{-1}$ = 1 dyn cm^2 stat coloumb^{-1}; e is the electronic charge in an ion pair; d is the distance between the centers of positive and negative charge in an ion pair; and k' is a parameter related to the electrostatic energy per ion pair released upon cluster collapse. As previously mentioned, the magnitude of k' depends on the cluster geometry and so a particular cluster structure must be assumed to calculate n.

A similar theory of multiplets and clusters has been developed by Dreyfus.[49,50] Again starting with the assumption of contact ion pairs,

multiplets are thought to occur with a maximum size determined by the steric hindrance of the surrounding non-ionic coating. The three main energies which are thought to control cluster formation are: 1) the residual electrostatic energy between multiplets, 2) the steric repulsion between monomers, and 3) the entropic energy needed to deform the coils. On the basis of these energies, the radius ρ_c of the cluster and the number of ion pairs η_c are calculated as:

$$\rho_c = l\left[\frac{e^2}{\kappa d k_B T}\right]^{3/(2j+1)} \frac{d^3}{jv} \tag{21}$$

$$\eta_c = \frac{2\pi d^6}{j^2 \sigma^3}\left[\frac{e^2}{\kappa d k_B T}\right]^{6/(2j+1)} \tag{22}$$

Where the polymer chains are modelled as freely jointed rods of length l and cross-section σ; v is the volume of one monomer; and j is the number of basic ion pairs in a multplet. Other symbols have the same meaning as previously defined. In the case of a polyethylene matrix, j=2 is shown to be the most probable value. Using this value of j leads to the following scaling predictions.

$$\rho_c \sim d^{2.4}\sigma^{-1} \tag{23}$$

$$\eta_c \sim d^{4.8}\sigma^{-3} \tag{24}$$

Dreyfus goes on to consider the spatial arrangement of the clusters. In order to deposit their charges inside the clusters, the segments of the chains have to be somewhat extended. This constraint is minimized by choosing a structure with the least distance between first neighbors for a given density of lattice sites. The diamond lattice is one simple structure which meets this criterion. Assuming such a lattice and requiring the conservation of charge leads to the following prediction for the distance D between first neighbor clusters:

$$D = 1.6(\rho_c{}^2 1)^{1/3} c^{-1/3} \qquad (25)$$

where c is the concentration of charged monomers.

Even though the distance D between clusters is quite large, a local order is nonetheless predicted. This surprising prediction is based on the fact that the clusters are linked by many segments whose average length cannot be easily extended to accomodate changes in D. This results in an entropic chain tension which holds the clusters locally on a regular lattice. Perhaps the most interesting aspect of this hypercrystal model is its implications for solvation. In the process of hydration, there is a strong tendency for the clusters to collapse into channels which, in the present model, would be along the tetrahedral bonds of the diamond lattice. The resulting three dimensional network, with appropriate consideration for lattice model artifacts, is of great

significance in understanding the cationic transport properties of ionomers.

An additional aspect of ionomer structure is the conformational behavior of the hydrocarbon chains. Eisenberg originally made the simplifying assumption that, on average, the chains would not undergo dimensional changes as a result of clustering of the ionic species. This restriction was later removed by Forsman[51] who showed that chain dimensions must actually increase as a result of ionic association, though the amount of such expansion will depend on the shape and symmetry of the cluster. The results of these calculations are embodied in the following equation.

$$\alpha^2 = \frac{\langle L^2 \rangle}{\langle L_o^2 \rangle} = 1 + \left[\frac{m}{CN} \right]^{2/3} \left[\frac{f}{M_o} \right]^{1/3} \frac{[1 + \psi(vf)^{2/3}]}{2k} \qquad (26)$$

where α is the expansion due to clustering; m is the number of interacting groups in a cluster; C is the concentration; k is the proportionality factor between the unperturbed mean end-to-end distance and the molecular weight; f is the fraction of repeat units participating in cluster formation; v is the volume fraction of polymer; and ψ is a dimensionless factor determined by the geometry of the clusters. This analysis assumes equally spaced interacting groups along a Gaussian backbone chain and clusters composed of a constant number of nearest neighbor groups. These theoretical predictions of chain

expansion have been confirmed by experimental measurements[32,52] on sodium salts of lightly sulfonated polystyrene.

The preceding theories comprise an excellent first approximation to the problem of ionomer structure by choosing solutions of salts in media of low dielectric constant as model systems. As Eisenberg points out, experimental and theoretical studies of such systems have shown that multiplets definitely exist. However, it may prove to be the case that the use of the contact ion pair as a fundamental structural unit is an oversimplification. More sophisticated theoretical treatment is clearly needed in the area of ionomer structure. It is possible that the coordinating tendency of the metal ions is of over-riding importance and that the fundamental structural units consist of metal ions coordinated to an appropriate number of anions. Certainly steric considerations severely limit the size of multiplets if they are of spherical geometry and if they are close packed. It is equally important, and a useful contribution of Eisenberg's work, to note that the steric limitations are relaxed if intervening hydrocarbon material is allowed in the structure. There can be little doubt that the size of the cluster is determined largely by the balance between electrostatic and elastic forces.

The current study investigates the thermal relaxation of these ionic associations in lightly sulfonated polystyrene ionomers. A

similar study of the viscoelastic properties of carboxylate-based polystyrene ionomers has been undertaken by Eisenberg and coworkers.[53-56] They observe that the glass transition temperature of styrene - sodium methacrylic acid copolymers monotonically increases as the salt group concentration rises from zero to nine mole percent. This regular rise in T_g implies that a constant fraction of the ionic material is dispersed in the continuous hydrocarbon phase. This dispersed material raises the glass transition temperature.

Stress relaxation experiments on these copolymers suggest a critical concentration above which the ionic aggregates join together to form clusters. For the styrene - sodium methacrylate copolymer system, this concentration is thought to be roughly six mole percent sodium methacrylate. Below this concentration, time-temperature superposition is obeyed but above six mole percent it is not possible to construct a master curve. The previously mentioned variation in T_g shows no sign of a discontinuity in the six mole percent range. This suggests that the onset of clustering does not significantly affect short range motions of the polystyrene matrix.

The dynamic mechanical properties of styrene-based ionomers have also been studied by Eisenberg and coworkers. Following the nomenclature of Deutsch et al.,[57] both an α and a β peak are observed in the loss tangent spectrum for materials containing less than six mole percent sodium methacrylate. Materials with higher contents of sodium

methacrylate exhibit broader β peaks and only a continuous increase in the loss tangent at temperatures corresponding to the α relaxation. At low concentrations, where separation between the polar and nonpolar entities is thought to be incomplete, the α relaxation would be due to isolated ion pairs or quartets. At higher ionic contents where separation may be more complete, the α relaxation may arise from motions of the salt groups within larger associations or clusters.

The ionomer system to be investigated in this study is lightly sulfonated polystyrene. This material was developed by Makowski et al.[58,59] One comparison of this system and the previously mentioned styrene - sodium methacrylate system has been undertaken,[60] however the materials were not of matching molecular weight. As with the styrene - sodium methacrylate copolymers, two peaks are observed in the loss tangent spectrum of sulfonated polystyrene. The lower temperature peak is assigned to the glass relaxation of the ion-poor matrix. The higher temperature peak is attributed to a relaxation associated with the ionic regions. This latter relaxation occurs at markedly higher temperatures in the sulfonated polystyrene system than in the methacrylate copolymer. This implies that the sulfonate cluster is more stable than the carboxylate, as suggested by Lundberg et al.[61] The higher temperature relaxation is also present in the acid form when the acid content is roughly ten mole percent. This relaxation is relatively weak and occurs at lower temperatures than in the salt form. These materials may

contain some water which behaves as an ionic plasticizer, as described by Lundberg et al.[62]

In addition to plasticization effects, ionomer properties are determined by the choice of metal cation used for neutralization. In general, the presence of a metal salt species raises the glass transition temperature. Weiss and coworkers[63] report the opposite effect for sulfonated polystyrene neutralized with alkyl-substituted ammonium counterions. Mohajer and coworkers[64] have recently reported the effects of over-neutralization in a halato-telechelic polyisobutylene system. Physical properties such as modulus are dramatically affected by the presence of excess neutralizing agent. The variation in glass transition temperature can be controlled by the type and concentration of agent used. The need for precise neutralization levels is evident.

Another variable which affects ionomer properties is the thermal history of the material. Weiss[65] reports a reorganization of sulfonated polystyrene morphology as a consequence of electrostatic interactions between sulfonate groups. While this aging is expected to be quite slow below T_g, it may be significant at elevated temperatures. For this reason, a great deal of care must be used in preparing samples with comparable thermal histories.

At sufficiently high ionic content, the mechanical properties of sulfonated polystyrene are those of a phase separated material. This behavior can be explained by the two previously mentioned relaxation processes: first the relaxation associated with the glass transition of the matrix, and second the relaxation of the ionic structures. Both processes are significantly affected by ionic content, type of counterion, presence of plasticizer or excess neutralizing agent and thermal history. Recent mechanical studies of sulfonated polystyrene ionomers[66] confirm the presence of these two relaxations however the exact nature of the phase separation remains unclear. To address the issue of phase separation in ionomeric materials, a model system has been developed and studied. Lightly sulfonated polystyrene salts of known polydispersity have been thoroughly characterized by a combination of elemental analysis, thermogravimetric analysis (TGA), and small-angle x-ray scattering (SAXS). The presence of thermal relaxations has been determined by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). From the results, conclusions are drawn regarding the dependence of cluster formation upon molecular weight distribution, counterion, and ionic content.

EXPERIMENTAL

Sulfonated polystyrenes of varying sulfonate levels were made from both a broad molecular weight distribution material (Dow Styron 666) and a narrow molecular weight polymer (obtained from Polymer Laboratories Ltd). Osmometry and viscosity measurements of the narrow distribution material indicate a number average molecular weight of M_w = 115,000 and a polydispersiity of M_w/M_n = 1.04. Gel permeation chromatography results confirm this and show a M_w/M_n of 2.66 for the broad distribution material.

The sulfonated polymers were prepared by the Exxon Chemical Company following procedures described previously.[15,16] In general, these polymers were modified in 1,2-dichloroethane using acetyl sulfate as the sulfonating agent. Following reaction at 50°C, the polymers were neutralized with either sodium hydroxide or zinc acetate and precipitated into methanol. The solution was subsequently filtered and the polymer was isolated as either the free acid, the sodium salt, or the zinc salt depending on the neutralizing agent. The sulfonated polymer was air dried overnight in the hood and finally vacuum oven dried at 50-60°C for 6-7 hours. Each precipitated polymer was analyzed for sodium or zinc as well as sulfur.

The results of the elemental analysis indicated that each sample was fully neutralized. The presence of excess neutralizing agent was corrected by repeated methanol washes. Even at the higher sulfonation levels, these materials remain reasonably stoichiometric. The sulfonated polystyrenes ranged in sulfonate content from about 1.0 to 7.5 mole percent. In this nomenclature, sulfonate content is based on the average number of repeat units of the polymer chain. Therefore, in the case of polystyrene, 1 mole percent refers to an average of one out of every hundred repeat units functionalized. A listing of the resulting materials is given in Table 12.

Gel permeation chromatography was performed on the sulfonated polymers using a Waters instrument and tetrahydrofuran as the eluent. The resulting chromatograms showed that no crosslinking had occured as a side reaction of the sulfonation process.

Thermogravimetric analysis was done using a Perkin-Elmer TGS-2 Thermogravimetric Analyzer and Electrobalance. Measurements were performed at a rate of 10^{o}C/minute throughout a temperature range of 50 to 500^{o}C. Repeated measurements were made to ensure reproducibility. Weight loss was recorded with an accuracy of ± 0.08 mg. Materials were analyzed in their powder form.

Films for use in the x-ray scattering experiments and the dynamic mechanical tests were prepared by compression molding under vacuum.

Table 12. Sulfonated Polystyrene Ionomers Studied in Bulk.

A. Ionomers Based on Dow Styron 666;
Mn = 83,000; Mw/Mn = 2.66

Exxon ID	Wt%S	Mol%S	Mol%Na	Mol%Zn	%Neut
4091-108A	0.13	0.43	----	----	---
4091-108A-1	0.33	1.08	0.46	----	194
4091-108A-2	0.17	0.55	----	0.29	171
4091-129	0.42	1.36	----	----	---
4091-129-1	0.35	1.12	0.40	----	159
4091-129-2	0.37	1.20	----	0.66	175
4091-108B	0.74	2.46	----	----	---
4091-108B-1	0.80	2.68	0.66	----	115
4091-108B-2	0.71	2.35	----	0.89	123
4091-134	1.15	3.87	----	----	---
4091-134-1	1.34	4.54	2.13	----	222
4091-134-2	1.24	4.19	----	2.20	174

B. Ionomers Based on Polymer Laboratories Material;
Mn=115,000, Mw/Mn=1.04

Exxon ID	Wt%S	Mol%S	Mol%Na	Mol%Zn	%Neut
4091-130	0.39	1.29	----	----	---
4091-130-1	0.41	1.35	0.42	----	143
4091-130-2	0.39	1.28	----	0.57	143
4091-108E	0.72	2.37	----	----	---
4091-108E	0.75	2.49	----	----	---
4091-108E-1	0.83	2.76	0.63	----	---
4091-108E-2	0.76	2.53	----	1.09	141
4091-132	1.33	4.47	----	----	---
4091-132-1	1.37	4.66	1.90	----	193
4091-132-2	1.26	4.26	----	2.42	188

Pressing temperatures ranged between 200 and 280^{o}C depending on the counterion. All of the pressed films were allowed to cool as slowly as possible so as to approach equilibrium conditions. Considerable care was used to ensure comparable thermal histories for all samples. Solubility measurements were made after pressing to verify that thermally induced degradation and crosslinking were absent.

Small-angle x-ray scattering measurements were performed using a Siemens x-ray generator and Kratky camera with slit collimation.. CuKα radiation was used in conjunction with a nickel filter. Typical generator settings were 40 kV and 25 mA. A Braun one-dimensional position sensitive detector and Canberra 35 multichannel analyzer were used. Conventional background corrections were made. It is a genuine pleasure to acknowledge D. Gobran for his expert assistance and for providing these measurements.

These ionomers were thermally characterized by differential scanning calorimetry using a Perkin-Elmer DSC-2. Measurements of dq/dt were made on specimens of about 5 mg mass, mechanically sealed in aluminum pans. The instrument was calibrated with standard reference materials and care was taken to establish baselines from far below to well above the transition of interest. The transition temperature was determined from the measured curves by the peak onset. Conventional conditioning methods and scanning rates of 20^{o}C/minute were used;

repeated experiments showed an accuracy of ± 2°C in the transition temperature measurements.

Dynamic mechanical thermal analysis was performed with a Polymer Laboratories Ltd DMTA. This instrument maintains an oscillating small strain using a dual cantilever bending mode. The loss and storage components of the dynamic modulus were recorded as a function of temperature. Scanning rates of 2°C/minute were used to investigate the mechanical response of these materials over a temperature range of -100 to 300°C. Frequencies between 0.33 and 30 Hz were employed. Reproducibility was ensured by replicate measurements. The resulting modulus values were calibrated by measuring the room-temperature modulus of a standard material both on the DMTA instrument and more precisely on a Dynastat machine. Once the true glassy modulus was determined, the absolute modulus curves were routinely calibrated to that correct value.

The author is grateful to M. Vratsanos for providing the Dynastat measurements.

RESULTS AND DISCUSSION

Characterization

Thermogravimetric analysis (TGA) of lightly sulfonated polystyrene ionomers was performed to determine a safe range of processing temperatures. This method measures the onset of thermal degradation by changes in weight. The temperatures at which weight loss occurs in these materials are summarized in Table 13. The results show that these materials are at least as thermally stabile as the unmodified precursor. A small change in weight is observed in the vicinity of 100°C in the salt forms. This is attributed ot the evolution of water. The problem of adsorbed water in ionomers is a widespread one.[67-69] From these TGA results, it was decided that the acid forms could be pressed at 200°C and the salt forms at 275°C without danger of thermal degradation.

Small-angle x-ray scattering (SAXS) measurements were performed on the sodium salts of these sulfonated polystyrenes. It has been noted[70] that ionomer SAXS patterns are very sensitive to sample history. As described in the preceding section, great care has been taken in this study to prepare samples of comparable thermal history. Typical scattering patterns for these materials are given in Figure 29. The results for these narrow molecular weight distribution materials are in

Table 13. Temperatures (^{o}C) of Weight Loss for Sulfonated Polystyrene Ionomers.

Mn = 83,000; Mw/Mn = 2.66

Sulfonation Level	Counterion H	Na	Zn
4.5 mol%S	100; 350	100; 320	90; 365
2.5	360	320	355
1.3	360	320	340
unmodified PS	-------300 ^{o}C----------		

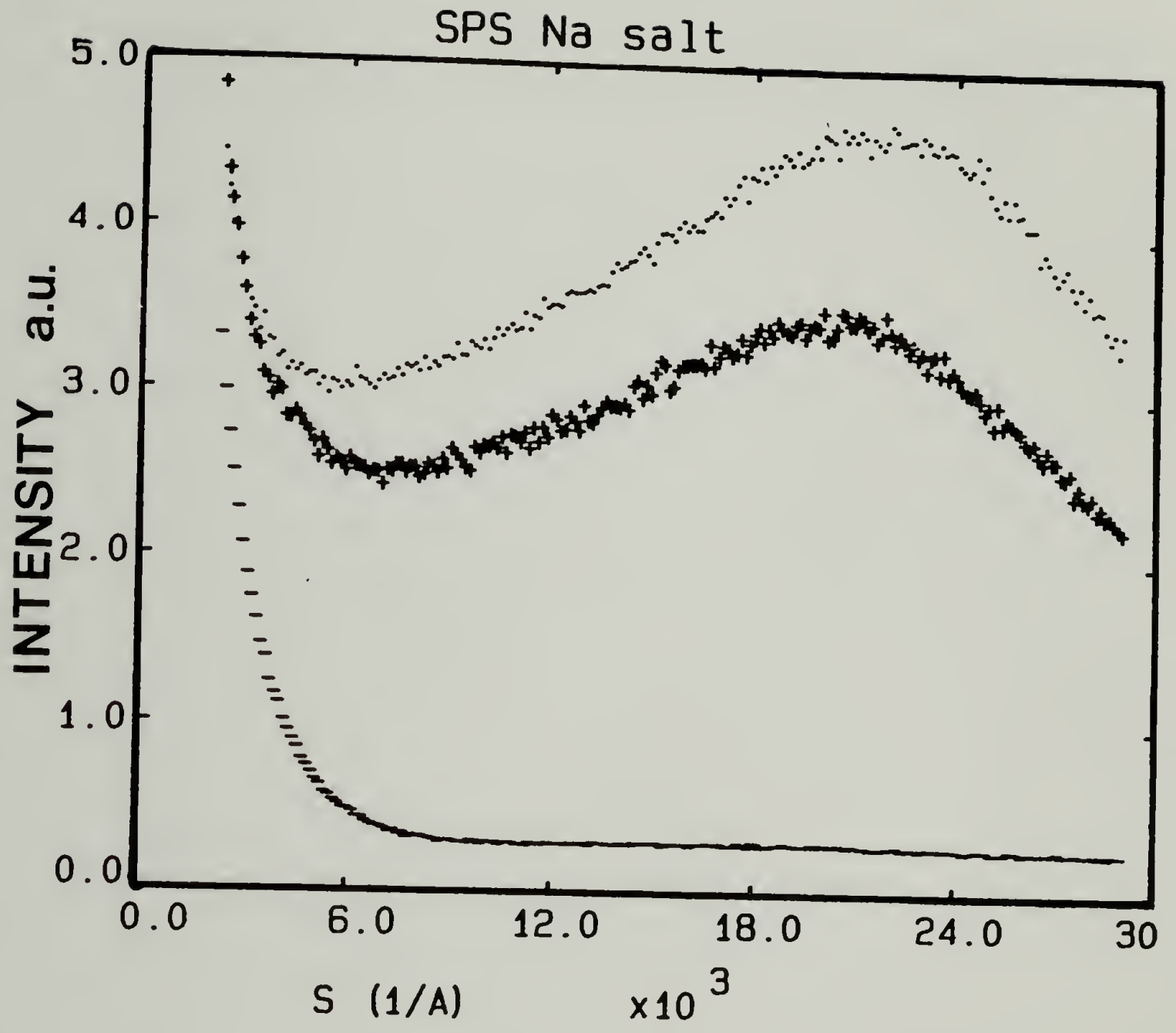

Figure 29. Small-angle x-ray scattering data for Na salts of sulfonated polystyrene (• = 4.5 mol%S with Mw/Mn = 1.04; + = 4.5 mol%S with Mw/Mn = 2.66; - = 1.3 mol%S with Mw/Mn = 1.04). Intensities smeared by slit collimation.

good agreement with previous measurements on sulfonated polystyrene ionomers of broad distribution.[71] This suggests that the solid state morphology of these ionomers is not strongly affected by polydispersity of the polymer backbone.

The SAXS patterns in Figure 29 show the expected "ionomer peak". This feature is characteristic of ionomeric materials, being present in nearly all ionomers regardless of the presence or absence of backbone crystallinity. It is well known that the interpretation of any scattering data is model dependent. The procedure is to assume a reasonable model, fit the experimentally observed data and deduce model parameters from the best fit. Several models for the distribution of salt groups in ionomers have been proposed based mainly on analysis of the ionomer peak. Those appearing up to 1979 are summarized in reference (4). The existing models are effectively based on two different approaches: either 1) the ionomer peak arises from structure within a scattering entity or 2) the peak is due to interference effects between scatterers.

Representative of the first approach is the "shell-core" model[72] originally proposed in 1974 and later elaborated.[73,74] In essence, the shell-core model postulates that in the dry state a cluster of ~0.1 nm in radius is shielded from surrounding unincorporated matrix ions by a shell of hydrocarbon chains. The surrounding matrix ions are attracted to the cluster by electrostatic forces but cannot approach more closely

than the outside of the hydrocarbon shell. This mechanism establishes a preferred distance between the cluster and the matrix ions. This distance is assumed to be on the order of 2 to 5 nm and accounts for the spacing of the ionomer peak. As a consequence of swelling and deformation studies, this model was refined to allow for either ion-depleted zones or lamellar geometries. The assumption of lamellar structures proves particularly interesting as it allows for non-spherical ionic domains which may extend over large regions of the material.

In the interference model, it is assumed that the ionomer peak arises from an interparticle distance. Recently, Yarusso and Cooper[75] have proposed a new interpretation of the ionomer peak which is based on the liquid-like scattering from hard spheres originally described by Fournet.[76] The Fournet model was quantitatively capable of fitting the x-ray peak from sulfonated polystyrene ionomers. In the case of zinc-neutralized material, about half of the ionic groups were found to aggregate in well-ordered domains ("clusters") with the remainder dispersed in the matrix ("multiplets"). The clusters had an estimated diameter of 2.0 nm and their distance of closest approach was found to be 3.4 nm center-to-center. It is clear that this model, although based on quite different physical principles, yields structural parameters which are very similar to those obtained from the shell-core model and which are consistent with what may be termed the "standard" model for ionomer structure of multiplets and clusters.

If the peak in Figure 29 is ascribed to a cluster spacing, then a Bragg distance of approximately 45 A is calculated. The disappearance of the ionomer peak below a certain ionic content (between 1.3 and 4.5 mole percent sulfonation in this case) has been used to argue the presence of a critical ionic content.[53] Below this critical level, the ionic species are thought to occur as multiplets while clusters form above the critical ionic concentration.

Relaxations and Transitions

The temperature of the glass transition T_g in these model ionomers was measured by differential scanning calorimetry (DSC). Typical results appear in Figure 30 and are summarized in Table 14. It should be noted that the glass transition temperature is insensitive to molecular weight distribution at the higher sulfonation levels. Figure 31 shows the transition temperatures of the SPS ionomers. The T_g of the ionomer is a function of ionic content. The increase in T_g for the sodium salt is approximately $2^{\circ}C/(mol\%$ of ions). Interestingly, this is the same value reported for styrene - sodium methacrylate copolymers.[54] The zinc salt exhibits a much higher value on the order of $5^{\circ}C/mol\%$. This effect is too large to be attributed to increased chain stiffness caused by the inclusion of ionic groups along the polymer backbone. Therefore the increase in T_g must be due to the presence of ionic material dispersed in the hydrocarbon matrix. DSC proved insensitive to

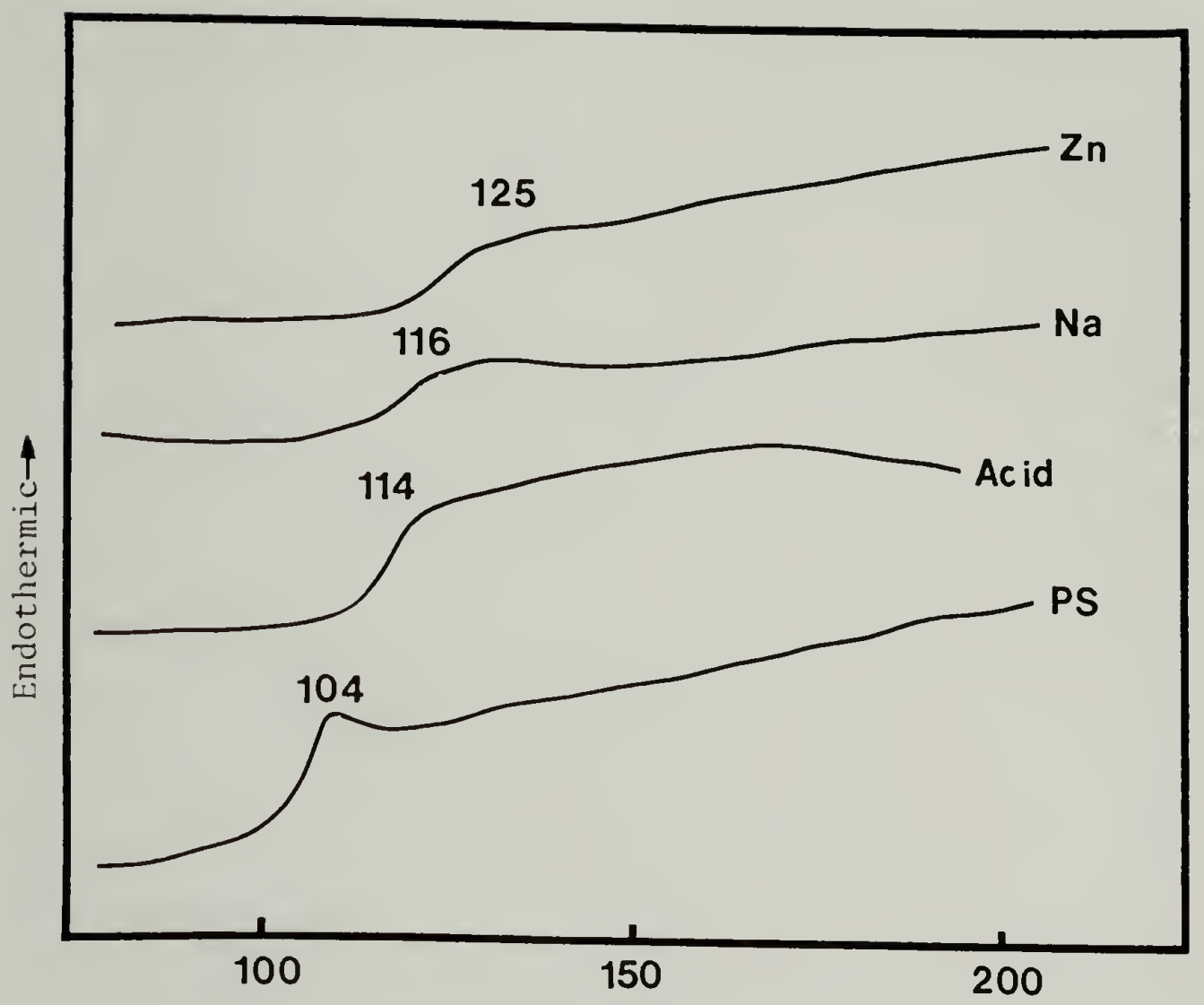

Figure 30. Differential scanning calorimetry data for Na salts of sulfonated polystyrene (115,000 g/mol; 4.5 mol%S).

Table 14. Variation in Glass Transition Temperatures (^{o}C) of Sulfonated Polystyrene Ionomers.

Mn = 83,000; Mw/Mn = 2.66

Sulfonation Level	Counterion H	Na	Zn
4.5 mol%S	114	116	125
2.5	110	112	116
1.3	107	110	110
unmodified PS	-----104^{o}C----------		
4.5 (Mw/Mn=1.04)	114	117	125

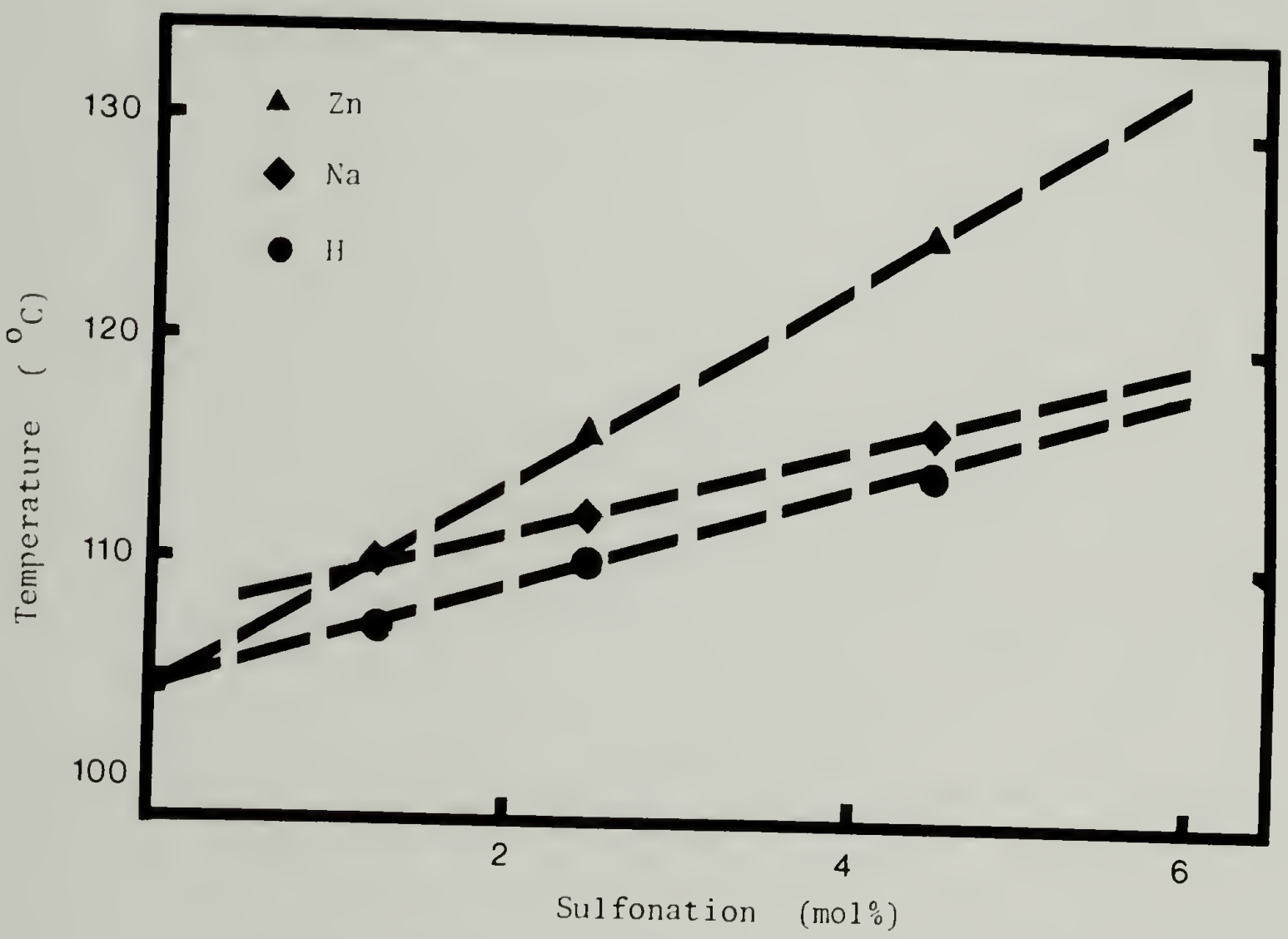

Figure 31. Variation in glass transition temperature with ionic content for sulfonated polystyrene (115,000 g/mol).

higher temperature relaxations and so dynamic mechanical thermal analysis (DMTA) was performed to extend the range of measurement.

DMTA measurements were made on materials of broad and of narrow molecular weight distribution. In these measurements, the dynamic modulus is measured as a function of temperature T and frequency τ. This quantity is related to the storage modulus E' and the loss modulus E" by:

$$E(t,\tau) = E'(T,\tau) + iE"(T,\tau) \qquad (27)$$

An additional experimental quantity is the loss tangent which is defined as:

$$\tan \delta = E"/E' \qquad (28)$$

In the vicinity of a molecular relaxation, the storage modulus will drop dramatically while the loss tangent and storage modulus exhibit maxima. In this study, a range of frequencies between 0.33 and 30 Hz was studied. Typical moduli and tan δ results are shown in Figures 32 - 34. Two relaxations are readily apparent and are labelled α and β in decreasing temperature. The mechanical spectrum was also measured between -100 and 50^{o}C but no other relaxations were observed.

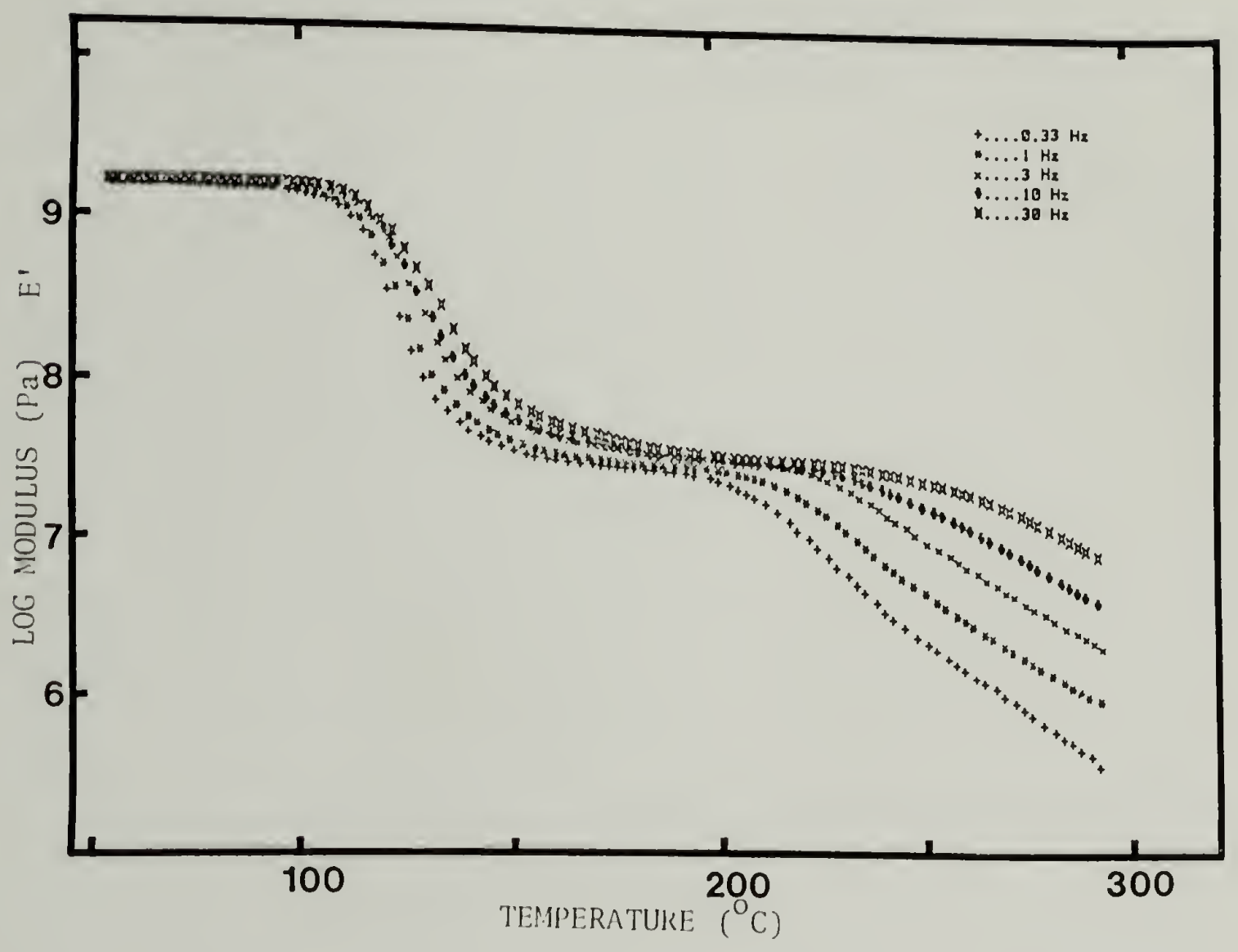

Figure 32. Storage modulus as a function of temperature and frequency for sulfonated polystyrene (115,000 g/mol; 7.5 mol%S).

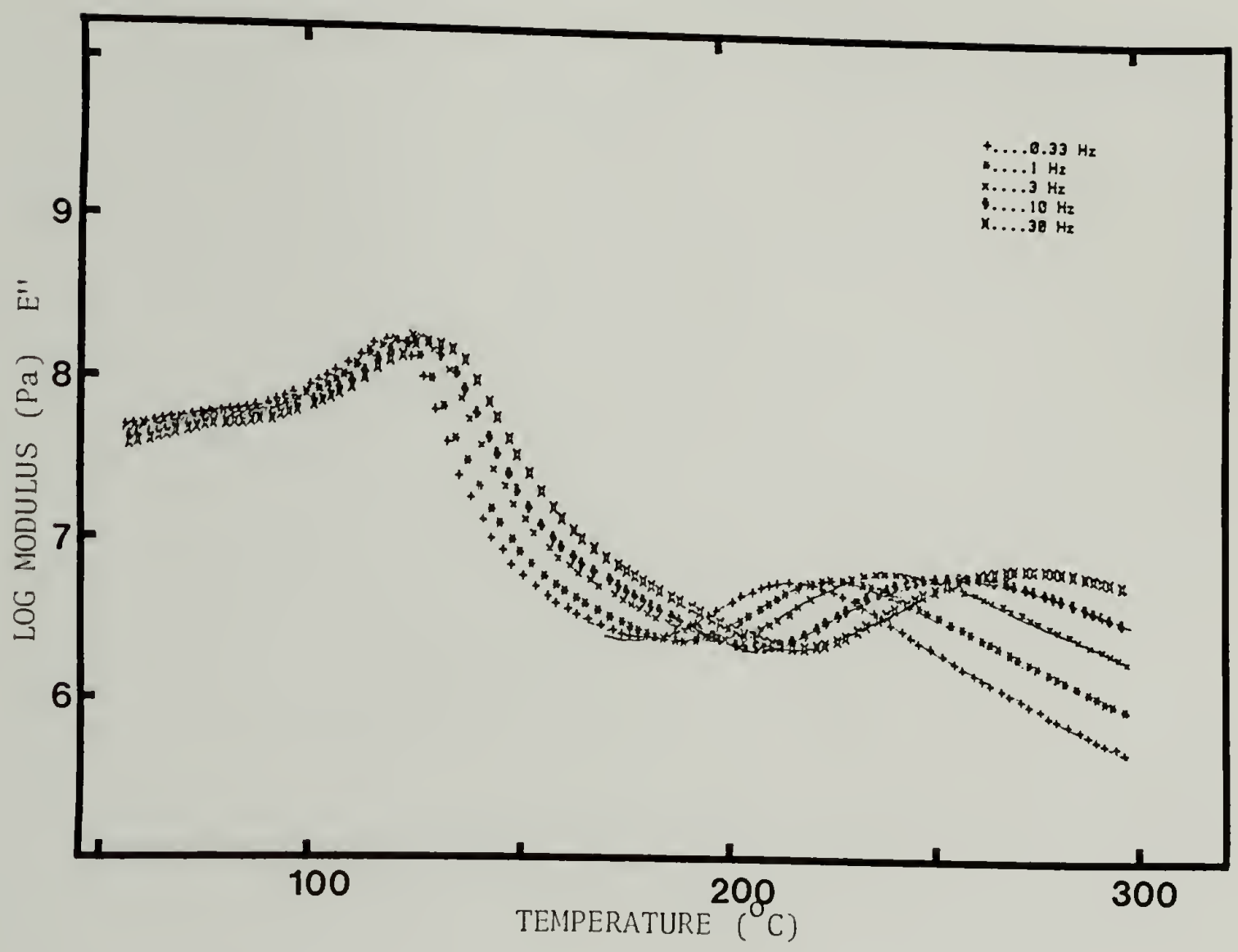

Figure 33. Loss modulus as a function of temperature and frequency for sulfonated polystyrene (115,000 g/mol; 7.5 mol%S).

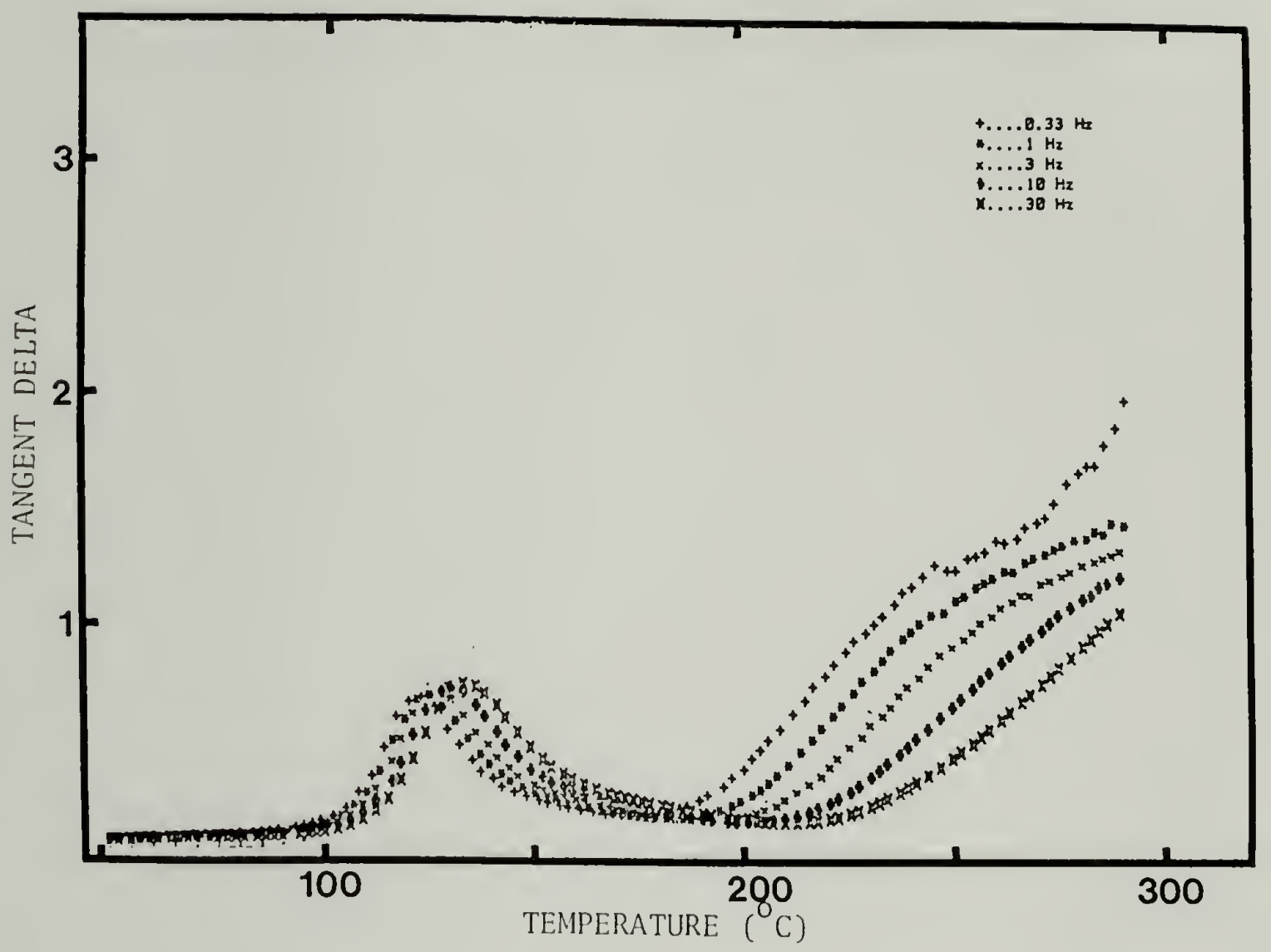

Figure 34. Tangent delta as a function of temperature and frequency for sulfonated polystyrene (115,000 g/mol; 7.5 mol%S).

The activation energy E_{act} of a relaxation can be calculated from its variation with frequency. This is done via the well-known Arrenhenius relation

$$\log(\tau) \sim \frac{-E_{act}}{2.303\ kT} \tag{29}$$

where kT is thermal energy. A typical Arrhenius plot is shown in Figure 35 and the activation energies of the β relaxation are summarized in Table 15. It is especially clear in the narrow distribution materials that the addition of ionic groups raises the activation energy of the β relaxation. This mechanical relaxation is attributed to the onset of motion which accompanies the glass transition. These activation energy values are consistent with the DSC results.

Each of the mechanical spectra shown in Figures 36 - 41 exhibit both α and β relaxations. For the sake of clarity, experimental points are omitted from the curves. Scatter in these data is comparable to that in Figure 34. The lower temperature β relaxation (attributed to the matrix T_g) increases systematically with increasing ionic content. This is in good agreement with the DSC measurements of T_g. When the tan δ curves are examined carefully, it can be seen that the materials of broad molecular weight distribution exhibit broader β relaxation peaks than do those of narrow distribution. This is doubtlessly due to the wider range of chain lengths present in the polydisperse samples. The β relaxation occurs at a significantly lower temperature in the

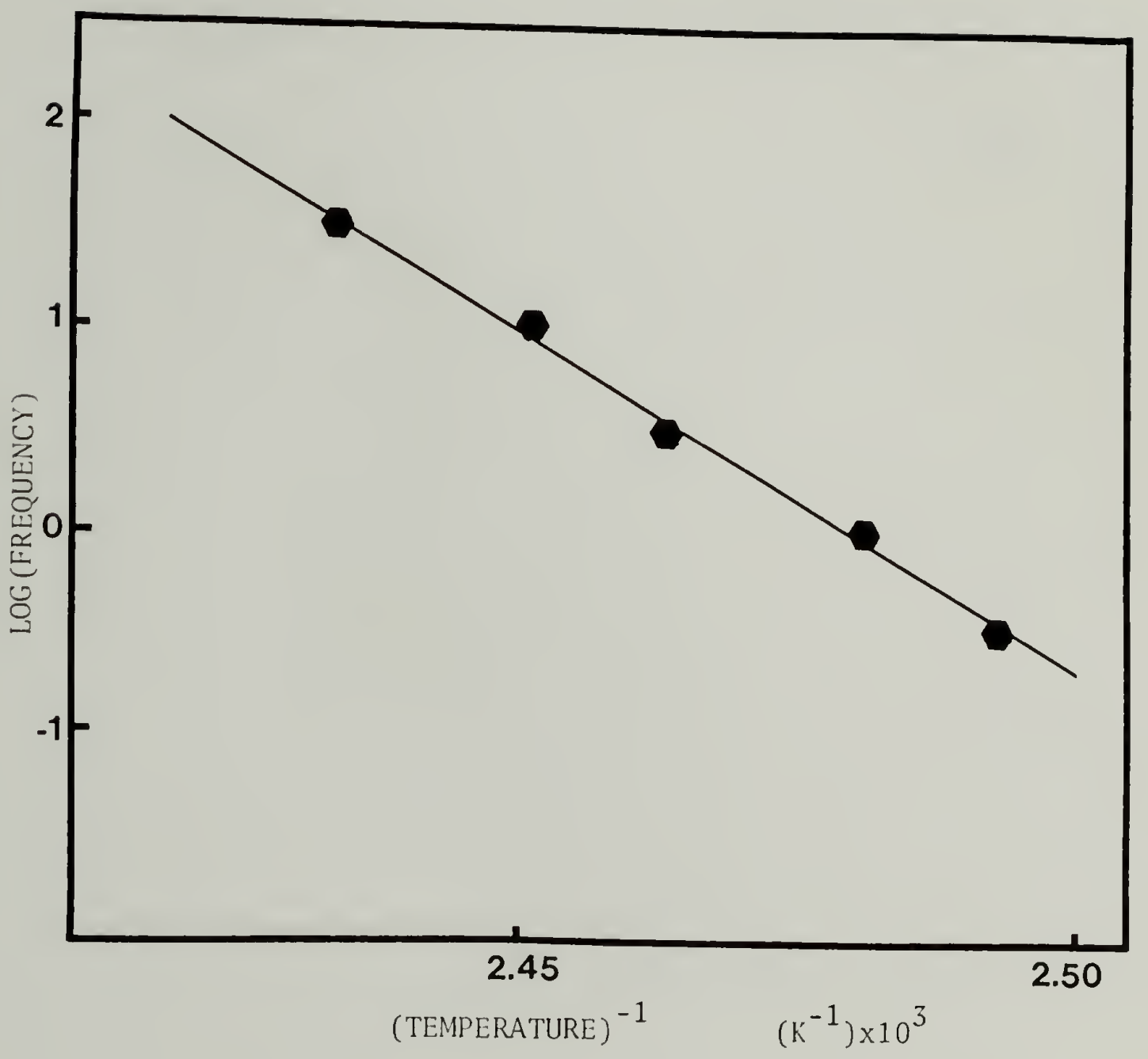

Figure 35. Arrhenius plot for sulfonated polystyrene (115,000 g/mol; 7.5 mol%S).

Table 15. Activation Energies (kJ/mol) of the β Relaxation in Sulfonated Polystyrene Ionomers as Measured by DMTA

A. Mn = 83,000; Mw/Mn = 2.66

Sulfonation Level	Counterion H	Na	Zn
4.5 mol%S	427	430	492
2.5	561	416	541
1.3	561	453	463
unmodified PS	----418 kJ/mol----------		

B. Mn = 115,000; Mw/Mn = 1.04

Sulfonation Level	Counterion H	Na	Zn
4.5 mol%S	448	423	585
2.5	567	576	576
1.3	447	564	573
unmodified PS	----337 kJ/mol----------		

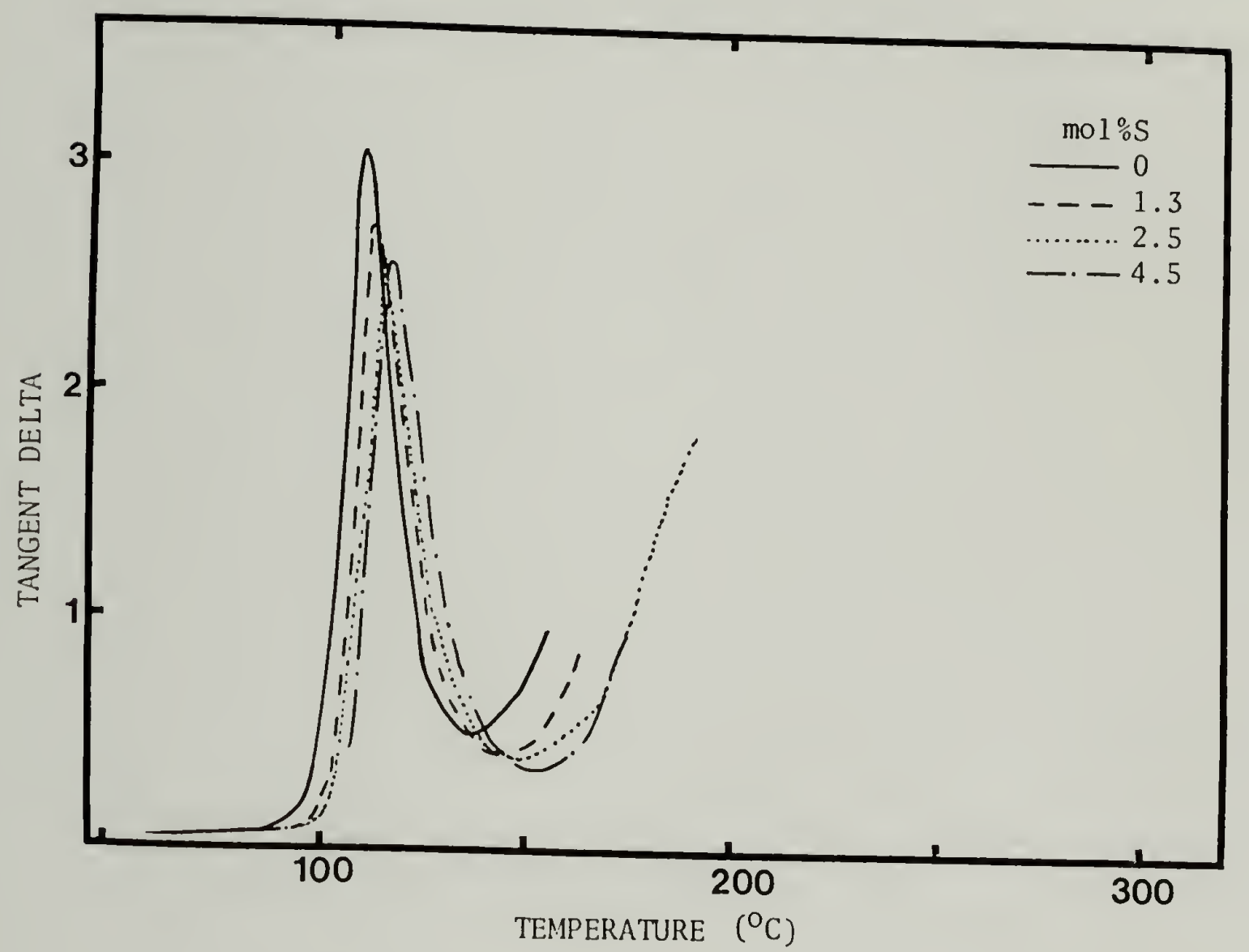

Figure 36. Tangent delta (1 Hz) as a function of temperature for acid forms of sulfonated polystyrene (115,000 g/mol with Mw/Mn = 1.04).

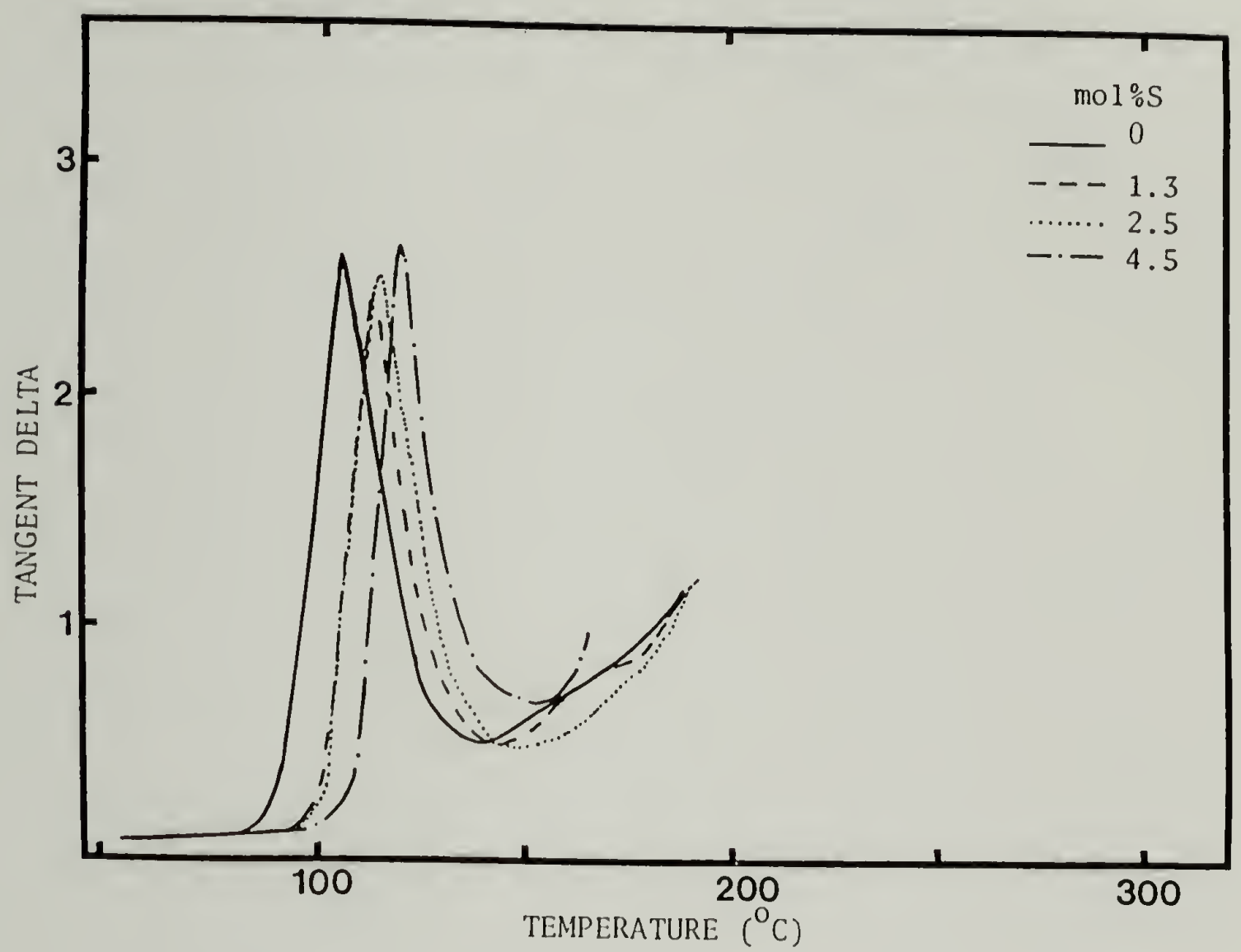

Figure 37. Tangent delta (1 Hz) as a function of temperature for acid forms of sulfonated polystyrene (83,000 g/mol with Mw/Mn = 2.66).

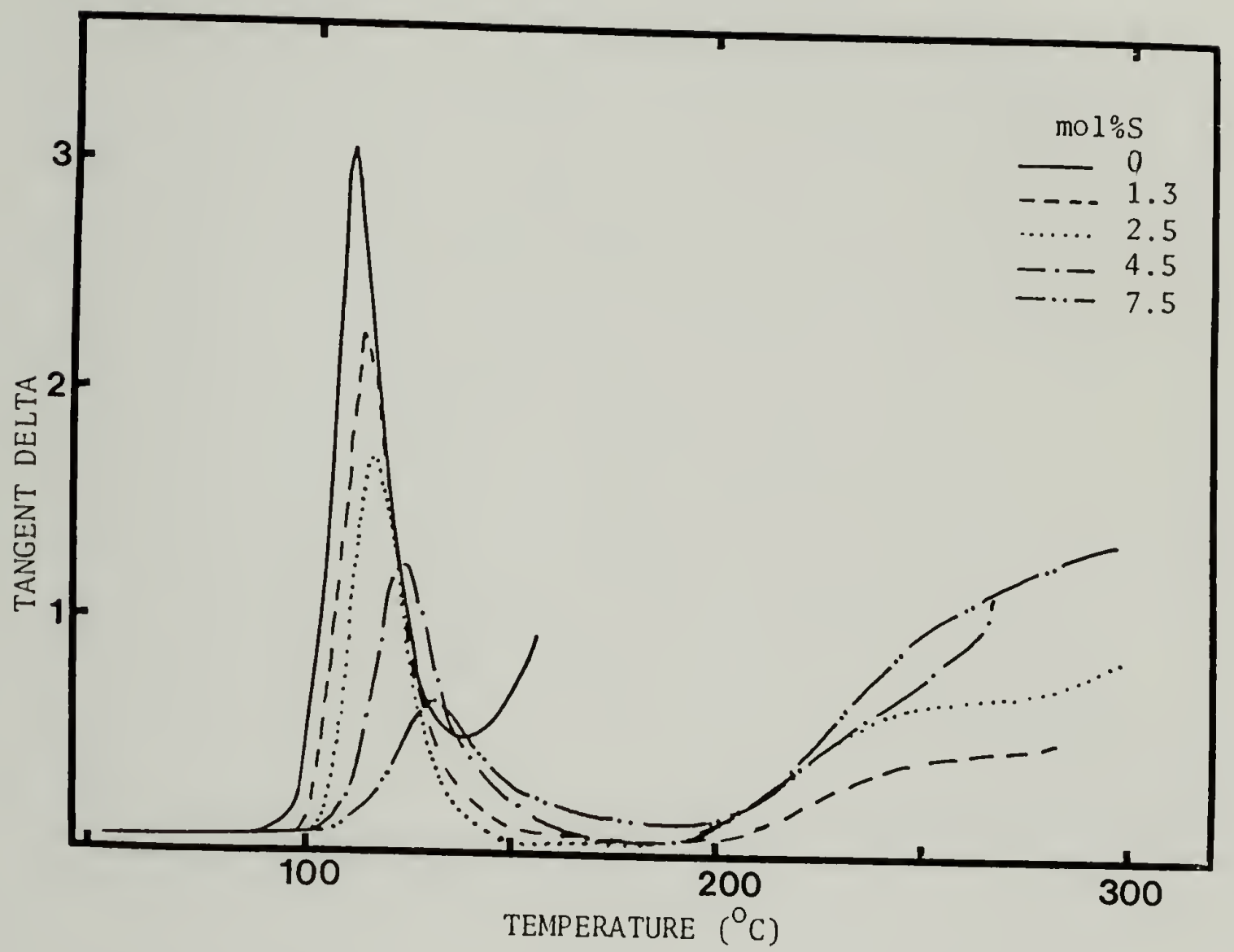

Figure 38. Tangent delta (1 Hz) as a function of temperature for Na salts of sulfonated polystyrene (115,000 g/mol with Mw/Mn = 1.04).

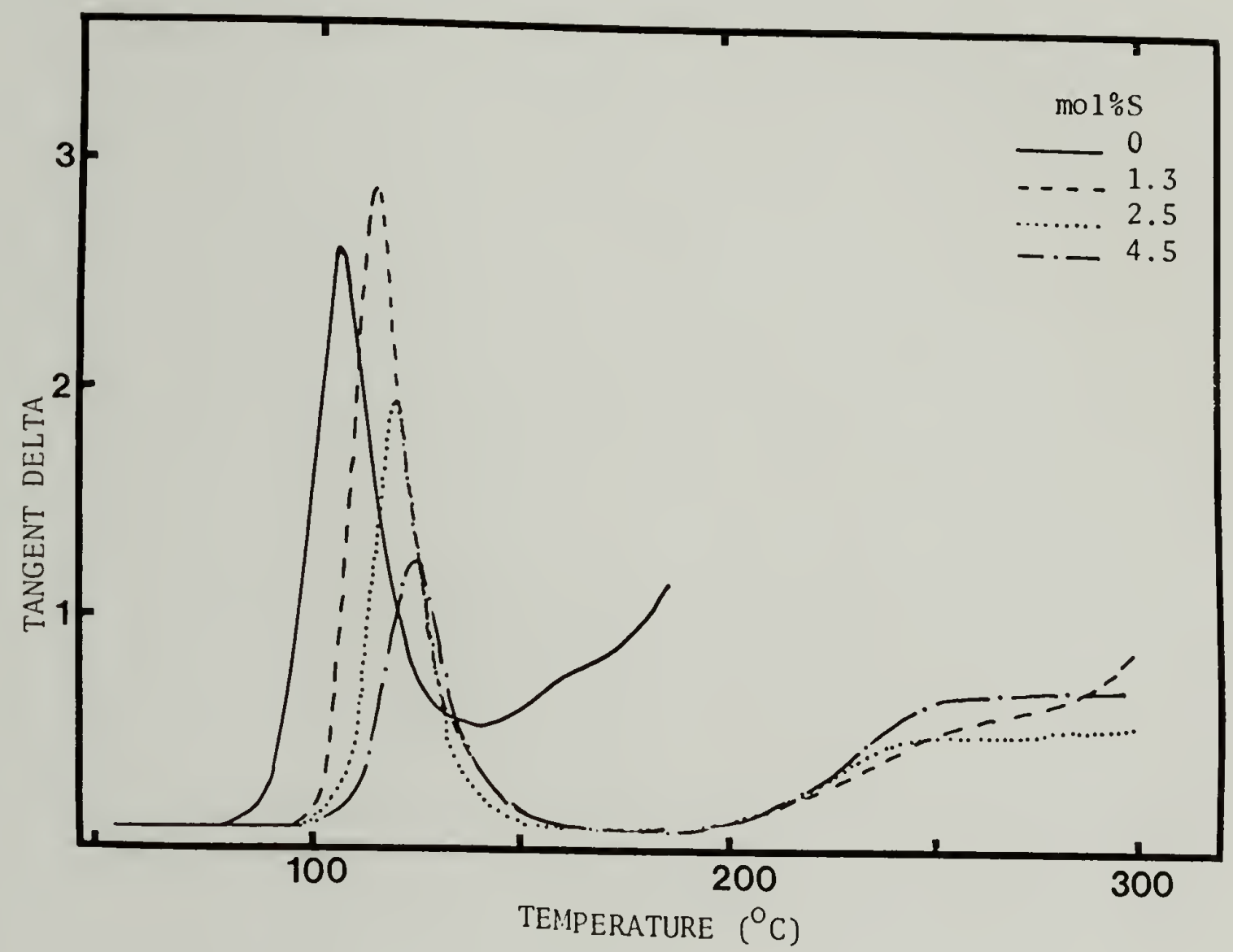

Figure 39. Tangent delta (1 Hz) as a function of temperature for Na salts of sulfonated polystyrene (83,000 g/mol with Mw/Mn = 2.66).

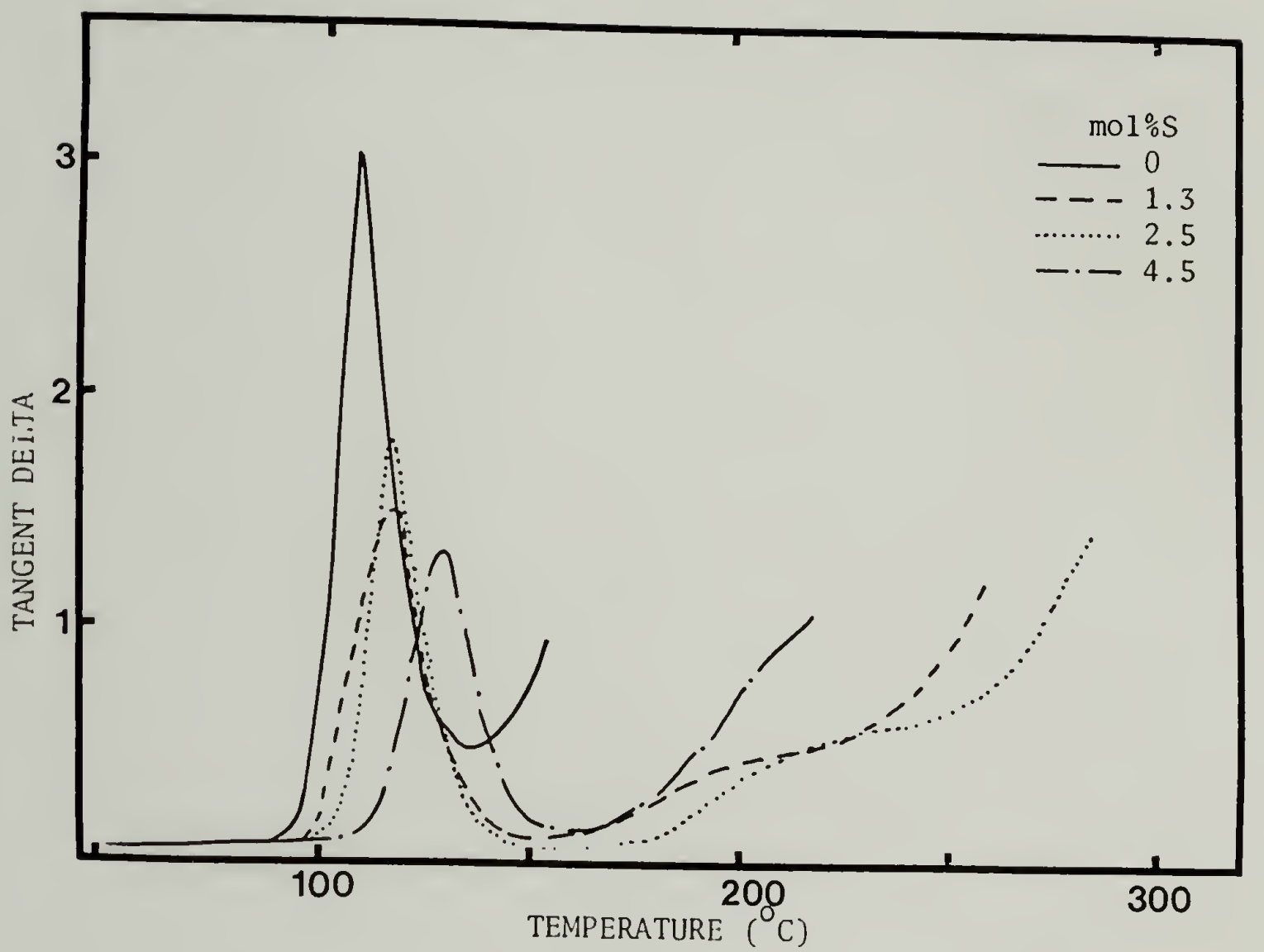

Figure 40. Tangent delta (1 Hz) as a function of temperature for Zn salts of sulfonated polystyrene (115,000 g/mol with Mw/Mn = 1.04).

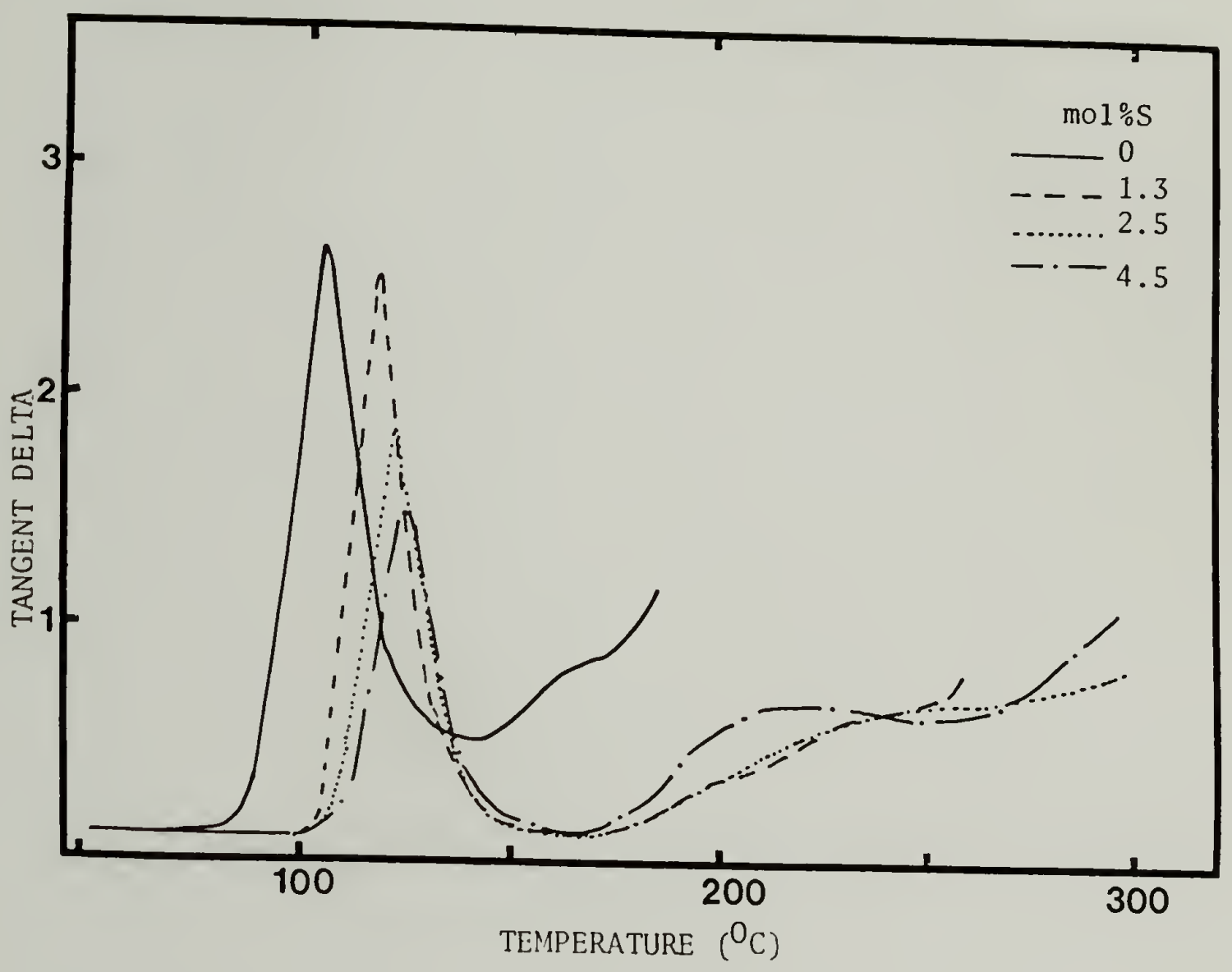

Figure 41. Tangent delta (1 Hz) as a function of temperature for Zn salts of sulfonated polystyrene (83,000 g/mol with Mw/Mn = 2.66).

narrow molecular weight distribution polystyrene than in the broad distribution material. This can be explained as a plasticization effect of the shorter chains. This effect diminishes with increasing ionic content, indicating that chain mobility is predominantly affected by the presence of ionic associations rather than polydispersity.

The α relaxation is also evident in Figures 36 - 41. Since the ionomer will flow under pressure at temperatures above the α relaxation, this relaxation is generally attributed to the break-up of the ionic multiplets. This relaxation is not observed in any of the acid forms; this indicates that ionic crosslinking is absent in the acid form at these sulfonation levels. When compared at the same ionic content, the zinc salt relaxes at lower temperatures than the sodium. The onset of this motion implies that zinc species are more weakly associated than sodium species. Similar effects have been reported for sodium and zinc salts of a different system.[77]

The presence of the α relaxation, even at these low ionic contents, is consistent with previous measurements on carboxylate-based polystyrene ionomers.[55] The α relaxation occurs at significantly higher temperatures in sulfonate-based materials than in the carboxylates though. This implies that the ionic interactions are stronger for the sulfonates. If this difference is true, then the sulfonate materials should have a lower critical concentration for clustering. Indeed, the data in Figure 29 suggest a critical concentration between 1.3 and 4.5

mole percent sulfonate groups whereas the critical concentration is not reached until 6 mole percent in the carboxylate case. These results show the importance of ionic type in determining the properties of ionomers.

CONCLUSIONS AND FUTURE WORK

A model ion-containing polymer system has been developed and thoroughly characterized. Specifically, lightly sulfonated polystyrene ionomers of both broad and narrow molecular weight distribution have been studied by elemental analysis, gel permeation chromatography, thermogravimetric analysis, and small-angle x-ray scattering. The presence of thermal transitions and relaxations has been determined by differential scanning calorimetry and dynamic mechanical thermal analysis. The effects of molecular weight distribution on thermal relaxations are found to be small for these ionomers. Clustering is absent in the acid form throughout the range of ionic contents studied. The presence of ionic groups in the polymer is shown to increase the glass transition temperature. The results reveal the presence of ionic associations in both zinc and sodium salts at all the ionic levels examined. These findings are consistent with earlier work on carboxylate-based polystyrene ionomers.

Clearly, several questions remain. The following studies are suggested to extend this investigation of sulfonated polystyrene ionomers in the solid state. To complete the comparison with carboxylate-based materials, stress relaxation measurements should be performed and the construction of master curves attempted. An

important variable in tensile properties of ionomers is the presence of ionic impurities. For this reason, quantitative studies should be made on the effects of overneutralization, water content, and the intentional addition of ionic plasticizers to the material. Dielectric relaxation measurements would be an important charactacterization method for these studies.

Thermal history effects have been shown to be important for ion-containing polymers. Similarly, solvent history should have an important effect in films prepared by solvent casting. Bearing in mind the findings of chapter I, films cast from ionizing and non-ionizing solvents should be studied.

Two important scattering measurements are also recommended. First, small-angle neutron scattering using the mixed labelling technique of chapter I should be performed on ionomers in the bulk state. Data should be gathered over a sufficient angular range to determine both the radius of gyration of a single chain and its persistence length. These measurements should be performed as a function of thermal and solvent histories as well as ionic content. The results would describe the local chain behavior in the vicinity of an ionic site as well as the overall chain conformation.

Secondly, cesium salts of narrow molecular weight distribution should be studied using a high intensity x-ray source. The low

polydispersity and carefully controlled sulfonation of these samples will decrease the breadth of the ionic cluster size distribution. The use of an intense source will allow the collection of precise data over a sufficient angular range to evaluate existing structural models. Again, these experiments should be performed on materials with a variety of ionic contents and sample histories. The results would clarify the nature of ionic structures in solid ionomers.

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